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Contributions from the Sheffield Laboratory of Yale College.

## XIII.—ON THE ALKALINITY AND DIASTATIC ACTION OF HUMAN SALIVA.

BY R. H. CHITTENDEN AND J. S. ELY.

It is well known that human mixed saliva ordinarily possesses an alkaline reaction; as to the degree of alkalinity, however, but little has hitherto been definitely known. The same is true of the saliva from animals; but recently Herter,<sup>1</sup> in an analysis of the submaxillary secretion from a dog, found .090 per cent. of sodium carbonate, and this in saliva obtained by irritating the mucous membrane of the mouth with acetic acid.

Recent experiments<sup>2</sup> have plainly demonstrated that the addition of small quantities of sodium carbonate to saliva greatly impairs its diastatic action. It has therefore seemed to us desirable to ascertain the amount of alkali present in normal mixed saliva, also whether the alkalinity is subject to variation in different persons and at different times, and if so, whether there is any connection between variations of alkalinity and the diastatic action of saliva.

The saliva examined was obtained from fourteen different persons, all of whom, with one exception, were men between the ages

<sup>1</sup> Published in Hoppe-Seyler's *Physiologische Chemie*, p. 192.

<sup>2</sup> This Journal, 3, 305; also 4, 121.

of twenty and thirty. The secretion of the saliva was accelerated by chewing a small piece of pure rubber. The saliva was collected generally an hour or two after breakfast, in quantities of 50 cc., and was at once filtered through paper in an atmosphere free from ammonia. A portion of the filtered fluid was then at once neutralized with a standard acid solution to determine the alkalinity, while another portion was used in the determination of the diastatic action. Great care was taken to have all the dishes used perfectly clean and dry, so that there might be no dilution or contamination of the saliva.

The method adopted in the determination of the alkalinity was as follows: 25 cc. of the filtered saliva were mixed with twenty drops of an alcoholic solution of cochineal and about 10 cc. of pure water, and then titrated directly with a dilute solution of hydrochloric acid in a room carefully guarded from ammoniacal fumes. The main difficulty attending the titration was the turbidity or precipitation produced in the saliva when the neutral point was nearly reached, thereby obscuring the change of color in the indicator. Cochineal was found to work to the best advantage; but as the precipitate produced by neutralization was insoluble in excess of acid, it made it difficult to use the perhaps better method of adding an excess of acid and then titrating back with standard alkali. The standard acid was made of such strength as to contain approximately .2 per cent. HCl. Titration with standard solution of silver nitrate showed that it actually contained .19 per cent. HCl, consequently 1 cc. of the standard acid was equivalent to .00276 gram  $\text{Na}_2\text{CO}_3$ .

A few determinations of the alkalinity of several specimens of saliva were then made to ascertain the amount of dilute acid required in a single determination, after which a standard solution of pure sodium carbonate was made of such strength that 1 cc. contained .0018292 gram  $\text{Na}_2\text{CO}_3$ . With this solution the dilute acid was standardized, under exactly the same conditions as the saliva was subjected to, with the following results:

12cc  $\text{Na}_2\text{CO}_3$  sol. required 7.87cc HCl sol., 1cc HCl sol. = .00278 gr  $\text{Na}_2\text{CO}_3$

|    |   |   |       |   |   |   |         |   |
|----|---|---|-------|---|---|---|---------|---|
| 12 | " | " | 7.87  | " | 1 | " | =.00278 | " |
| 8  | " | " | 5.17  | " | 1 | " | =.00281 | " |
| 12 | " | " | 7.67  | " | 1 | " | =.00286 | " |
| 12 | " | " | 7.78  | " | 1 | " | =.00280 | " |
| 24 | " | " | 15.69 | " | 1 | " | =.00279 | " |
| 24 | " | " | 15.69 | " | 1 | " | =.00279 | " |

Average, 1cc. standard HCl sol. = .00280 gram  $\text{Na}_2\text{CO}_3$ .

Calculated 1cc. " " = .00276 " " "

It is thus apparent that the error attending the use of such a dilute acid solution under these circumstances is inappreciable, and the results obtained in the analyses of the different samples of saliva may be looked upon as accurately expressing the degree of alkalinity.

The diastatic action of the saliva was determined in each case as follows: .5 gram of starch was heated to boiling with 40 cc. of water in a small flask, and when cold 12 cc. of the filtered saliva were added from an accurately calibrated burette, and the mixture placed at 40° C for 30 minutes. At the end of this time all further diastatic action was stopped by boiling the fluid. When cold, the mixture was diluted with water to 200 cc., and in 50 cc. or one-fourth of the filtered fluid, sugar was determined gravimetrically by the use of the method so carefully elaborated by Maercker<sup>1</sup> and others. From the weight of metallic copper, the amount of reducing substance calculated as dextrose was ascertained by the use of the reduction equivalents experimentally determined by Maercker.<sup>2</sup>

The following tables show the results obtained :

| Collector. | Time.   | Alkalinity.           |                                                 |              |                           | Diastatic Action.              |  |
|------------|---------|-----------------------|-------------------------------------------------|--------------|---------------------------|--------------------------------|--|
|            |         | HCl sol.<br>required. | Equivalent in Na <sub>2</sub> CO <sub>3</sub> . |              | Wt. Cu.<br>in one-fourth. | Percentage of<br>sugar formed. |  |
| A          | March 1 | 5.62 cc.              | .015736 gram.                                   | .063 per ct. | .1052 gram.               | 42.77 per ct.                  |  |
| "          | " 2     | 5.25 "                | .014700 "                                       | .059 "       | .1130 "                   | 45.94 "                        |  |
| "          | " 3     | 5.71 "                | .015988 "                                       | .064 "       | .1089 "                   | 44.28 "                        |  |
| "          | " 8     | 5.40 "                | .015120 "                                       | .061 "       | .1116 "                   | 45.37 "                        |  |
| "          | " 9     | 5.66 "                | .015848 "                                       | .063 "       | .1141 "                   | 46.39 "                        |  |
| "          | " 10    | 5.24 "                | .014672 "                                       | .058 "       | .1137 "                   | 46.23 "                        |  |
| " 3        | " 10    | 8.43 "                | .023604 "                                       | .094 "       | .1061 "                   | 43.14 "                        |  |
| "          | " 16    | 5.11 "                | .014308 "                                       | .057 "       | .1160 "                   | 47.26 "                        |  |
| "          | " 17    | 5.29 "                | .014812 "                                       | .059 "       | .1152 "                   | 46.93 "                        |  |
| "          | " 24    | 5.30 "                | .014840 "                                       | .059 "       | .1110 "                   | 45.13 "                        |  |
| "          | " 28    | 5.94 "                | .016632 "                                       | .066 "       | .1070 "                   | 43.51 "                        |  |
| " 3        | April 2 | 8.14 "                | .022792 "                                       | .091 "       | .1070 "                   | 43.51 "                        |  |
| Average.   |         |                       | .061 per ct. <sup>4</sup>                       |              |                           | 45.03 per ct.                  |  |

<sup>1</sup> Die Landwirthschaftliche Versuchs-Stationen, 25, 115-116; also this Journal, 3, 308.

<sup>2</sup> *Loc. cit.*

<sup>3</sup> Stood 12 hours before being examined.

<sup>4</sup> Exclusive of the two which stood 12 hours.

| Collector. | Time.    | Alkalinity.           |                                          |                           | Diastatic Action.         |                                |
|------------|----------|-----------------------|------------------------------------------|---------------------------|---------------------------|--------------------------------|
|            |          | HCl sol.<br>required. | Equivalent in $\text{Na}_2\text{CO}_3$ . |                           | Wt. Cu.<br>in one-fourth. | Percentage of<br>sugar formed. |
| B          | March 2  | 13.29 cc.             | .037212 gram.                            | .149 per ct.              | .1022 gram.               | 41.58 per ct.                  |
| "          | " 3      | 11.06 "               | .030968 "                                | .124 "                    | .1000 "                   | 40.66 "                        |
| "          | " 9      | 13.77 "               | .038556 "                                | .154 "                    | .0974 "                   | 39.63 "                        |
| "          | " 24     | 14.59 "               | .040252 "                                | .163 "                    | .1194 "                   | 48.64 "                        |
| "          | " 31     | 11.78 "               | .031144 "                                | .132 "                    | Lost.                     |                                |
| "          | April 2  | 11.64 "               | .032592 "                                | .130 "                    | .1018 "                   | 41.42 "                        |
| Average.   |          |                       |                                          | .144 per ct. <sup>2</sup> |                           | 42.38 per ct.                  |
| C          | March 2  | 5.01 cc.              | .014028 gram.                            | .056 per ct.              | .1062 gram.               | 43.18 per ct.                  |
| "          | " 3      | 4.67 "                | .031076 "                                | .052 "                    | .1020 "                   | 41.50 "                        |
| "          | " 10     | 5.16 "                | .014448 "                                | .058 "                    | .1050 "                   | 42.69 "                        |
| "          | " 10     | 5.00 "                | .014000 "                                | .056 "                    | Lost.                     |                                |
| "          | " 17     | 4.57 "                | .012796 "                                | .051 "                    | Lost.                     |                                |
| "          | " 28     | 8.50 "                | .023800 "                                | .095 "                    | .1026 "                   | 41.74 "                        |
| Average.   |          |                       |                                          | .062 per ct. <sup>2</sup> |                           | 42.27 per ct.                  |
| D          | March 2  | 5.81 cc.              | .016268 gram.                            | .065 per ct.              | .1083 gram.               | 44.04 per ct.                  |
| "          | " 9      | 7.47 "                | .020916 "                                | .084 "                    | .1069 "                   | 43.46 "                        |
| "          | " 16     | 6.95 "                | .019460 "                                | .078 "                    | .1095 "                   | 44.52 "                        |
| "          | " 17     | 7.26 "                | .020328 "                                | .081 "                    | .1058 "                   | 42.94 "                        |
| "          | " 24     | 8.41 "                | .023548 "                                | .094 "                    | .1010 "                   | 41.09 "                        |
| "          | " 28     | 4.81 "                | .013468 "                                | .054 "                    | .1029 "                   | 41.86 "                        |
| Average.   |          |                       |                                          | .076 per ct.              |                           | 42.98 per ct.                  |
| E          | March 2  | 6.79 cc.              | .019012 gram.                            | .076 per ct.              | .1062 gram.               | 43.18 per ct.                  |
| "          | " 17     | 8.18 "                | .022994 "                                | .092 "                    | .1071 "                   | 43.55 "                        |
| "          | " 24     | 7.52 "                | .021056 "                                | .084 "                    | .1268 <sup>3</sup> "      | 51.91 "                        |
| "          | " 28     | 7.33 "                | .020524 "                                | .082 "                    | .1029 "                   | 41.86 "                        |
| Average.   |          |                       |                                          | .083 per ct.              |                           | 45.12 per ct.                  |
| F          | March 10 | 7.17 cc.              | .020076 gram.                            | .080 per ct.              | .1014 gram.               | 41.25 per ct.                  |
| "          | " 10     | 7.47 "                | .020916 "                                | .084 "                    | .0991 "                   | 40.32 "                        |
| "          | " 16     | 7.34 "                | .020552 "                                | .082 "                    | .0995 "                   | 40.52 "                        |
| "          | " 17     | 7.70 "                | .021560 "                                | .086 "                    | .0961 "                   | 39.10 "                        |
| "          | " 28     | 6.64 "                | .018592 "                                | .074 "                    | .0961 "                   | 39.10 "                        |
| "          | " 31     | 7.79 "                | .021812 "                                | .087 "                    | .0946 "                   | 38.48 "                        |
| Average.   |          |                       |                                          | .082 per ct.              |                           | 39.79 per ct.                  |
| G          | March 16 | 9.83 cc.              | .027524 gram.                            | .110 per ct.              | .1056 gram.               | 42.93 per ct.                  |
| "          | " 17     | 8.72 "                | .024416 "                                | .097 "                    | .1028 "                   | 41.82 "                        |
| "          | " 28     | 9.86 "                | .027608 "                                | .110 "                    | .1029 "                   | 41.86 "                        |
| "          | " 31     | 9.29 "                | .026012 "                                | .104 "                    | .1015 "                   | 41.29 "                        |
| Average.   |          |                       |                                          | .105 per ct.              |                           | 41.97 per ct.                  |

<sup>1</sup> Stood 12 hours before being examined.<sup>2</sup> Exclusive of the one which stood 12 hours.<sup>3</sup> This result is probably too high, although no error in the analysis could be detected.



| Collector.     | Time.    | Alkalinity.        |                                          | Diastatic Action.      |                             |
|----------------|----------|--------------------|------------------------------------------|------------------------|-----------------------------|
|                |          | HCl sol. required. | Equivalent in $\text{Na}_2\text{CO}_3$ . | Wt. Cu. in one-fourth. | Percentage of sugar formed. |
| H              | March 24 | 5.24 cc.           | .014672 gram.                            | .059 per ct.           | .1054 gram.                 |
| "              | " 31     | 6.01 "             | .016828 "                                | .067 "                 | .1022 "                     |
|                | Average. |                    |                                          | .063 per ct.           | 42.21 per ct.               |
| I              | March 28 | 7.24 cc.           | .020272 gram.                            | .081 per ct.           | .1031 gram.                 |
| "              | " 31     | 3.30 "             | .009240 "                                | .037 "                 | .1016 "                     |
|                | Average. |                    |                                          | .059 per ct.           | 41.64 per ct.               |
| J              | March 28 | 8.77 cc.           | .024556 gram.                            | .098 per ct.           | .1011 gram.                 |
| "              | " 31     | 7.88 "             | .022064 "                                | .088 "                 | .0950 "                     |
|                | Average. |                    |                                          | .093 per ct.           | 39.89 per ct.               |
| K              | March 31 | 5.87 cc.           | .016436 gram.                            | .066 per ct.           | .1109 gram.                 |
| "              | April 3  | 5.53 "             | .015484 "                                | .062 "                 | .1107 "                     |
|                | Average. |                    |                                          | .064 per ct.           | 45.05 per ct.               |
| L              | March 31 | 7.06 cc.           | .019768 gram.                            | .079 per ct.           | .1017 gram.                 |
| "              | April 3  | 8.07 "             | .022596 "                                | .090 "                 | .1151 "                     |
|                | Average. |                    |                                          | .084 per ct.           | 44.13 per ct.               |
| M              | April 3  | 6.86 cc.           | .019208 gram.                            | .077 per ct.           | .1125 gram.                 |
| N <sup>1</sup> | " 2      | 7.06 "             | .019768 "                                | .079 "                 | .1016 "                     |
|                |          |                    |                                          |                        | 45.74 per ct.               |
|                |          |                    |                                          |                        | 41.33 "                     |

The average alkalinity for these 51 samples of saliva expressed in the form of sodium carbonate is .080 per cent. The average diastatic action of 54 samples of saliva expressed in the percentage of sugar formed from the starch is 42.82 per cent. A glance at the individual results obtained shows several interesting facts, which may be briefly summarized as follows:

1. Saliva from different individuals may show a constant difference in alkalinity as in A, B, F and G, although in the majority of cases the alkalinity varies only within narrow limits.
2. Saliva secreted by the same individual at different times has within certain limits a constant degree of alkalinity.
3. While saliva from different individuals shows in several cases a decided and constant difference in alkalinity, there is no corresponding difference in diastatic action which is at all constant. We are thus forced to the conclusion that the variations of alkalinity are within too narrow limits to exercise any appreciable influence on the diastatic action of the saliva.

<sup>1</sup> Stood 12 hours before being examined.

DETERMINATION OF ORGANIC MATTER IN  
POTABLE WATER.

BY PROF. J. W. MALLET, F. R. S.

*(Concluded from page 263.)*

## SANITARY CONCLUSIONS AND INTERPRETATION OF RESULTS.

To admit of easier comparison, the results by the chief processes examined have been thrown into graphical form in Tables XIX and XX, of which the former refers to the natural waters and the latter to those artificially prepared.

(These tables will appear with the general report.)

*Chemical results contrasted with actual sanitary history of the natural waters examined.*

I. An inspection of Table XIX shows that *no strongly marked generic difference is presented by the results from any of the processes for the estimation of organic matter or its elements between the generally wholesome waters of Class I and the medically condemned and fairly assumed as pernicious waters of Class II.* Judging by the general impression of the curves upon the eye, one would be inclined to attribute somewhat more importance to the results involving nitrogen than to those dependent upon carbon; but neither will afford the means of broadly distinguishing the two classes. This conclusion is otherwise illustrated by the figures in Table XXI.<sup>1</sup>

It will be seen from this table that no marked difference exists between the *highest, lowest or average* result obtained by any of the processes for the waters of Class I and the corresponding result for those of Class II. No one could, with these figures to guide him, refer a water of unknown origin to one or the other of the two classes on the evidence afforded by chemical analysis, using any or all of the processes in question. The most varied results presented in Class III admit of being studied with some interest in connection with the history of the individual waters, but are not available for the main purpose of testing the chemical methods, as this class includes only waters the sanitary character of which in advance of examination was more or less doubtful—waters under suspicion only.

<sup>1</sup> See next page.

TABLE XXI.— *Comparison of chemical results for waters of Classes I and II.*

|                                           | Least result. |           | Greatest result. |                   | Average. |                   |
|-------------------------------------------|---------------|-----------|------------------|-------------------|----------|-------------------|
|                                           | Class I.      | Class II. | Class I.         | Class II.         | Class I. | Class II.         |
| Organic carbon .....                      | .36           | .33       | 7.20             | 7.79              | 2.36     | 2.08              |
| Organic nitrogen .....                    | .08           | .03       | 1.41             | 6.88 <sup>1</sup> | .56      | .94 <sup>2</sup>  |
| Sum of organic carbon and nitrogen. ....  | .44           | .61       | 7.86             | 8.31 <sup>2</sup> | 2.92     | 2.92 <sup>2</sup> |
| Nitrogen of free ammonia. ....            | .008          | .008      | .675             | .295              | .092     | .090              |
| Nitrogen of albuminoid ammonia. ....      | .016          | .021      | .268+            | .214              | .112     | .099              |
| Nitrogen of total ammonia. ....           | .028          | .033      | .704             | .343              | .204     | .189              |
| Oxygen consumed in one hour (Tidy) .....  | .062          | .082      | 4.008            | 3.340             | .995     | .791              |
| Oxygen consumed in three hours (Tidy) ... | .210          | .104      | 5.212            | 4.188             | 1.305    | 1.065             |
| Oxygen consumed (Kubel). ....             | None.         | None.     | 7.443            | 6.000             | 2.140    | 1.271             |

2. Making the most liberal allowance for the imperfection of the different processes for the estimation of organic matter or its constituents, it is well worthy of notice how very small is the absolute amount of organic matter indicated as present in many of the most dangerous waters, an amount so small as to furnish important evidence against any chemical theory of the production of disease from this source, any theory based on the simple assumption that some of the chemical products of the decomposition of organic matter are poisonous or noxious in their effect upon the human system. Thus, if *the whole* of the organic carbon and nitrogen found in such waters as Nos. 35 and 36, of the highly dangerous character of which there can scarcely be a doubt, existed as strychnine, it would be necessary to drink about half a gallon of the water at once in order to swallow an average *medicinal* dose of the alkaloid. It is not easy to believe that the ptomaines, or any other chemical products of putrefactive change as yet observed, can possess an intensity of toxic power so very much greater than that of the most energetic of recognized poisons. While numerous facts

<sup>1</sup> This figure is undoubtedly too high, in consequence of incomplete reduction of nitrates. The next highest is 2.36, and even this is probably higher than the truth, for the same reason.

<sup>2</sup> Including the no doubt erroneous highest single figure.

go to support the belief that, not to the effect of any chemical substances (such effect necessarily standing in definite relation to their quantity), but to the presence of living organisms with their power of practically unlimited self-multiplication, we must in all probability look for an explanation of, most at any rate, of the mischief attributable to drinking water, it is of course possible that indirectly a large amount of organic matter in water may be more dangerous than a smaller quantity, as furnishing on a greater scale the suitable material and conditions for the development of noxious as well as harmless organisms.<sup>1</sup>

Whether variations in the mere quantity of organic matter, within such limits as occur in water at all likely to be used for drinking, are of much importance in this respect, *i. e.* as determinant of the presence or abundance of organisms, is a question which may be asked, and on it depends, I think, largely the utility of all attempts to determine or estimate the quantity of organic matter or its constituents as such.

3. A much more conspicuous difference between the waters of Classes I and II is presented by the results for nitrites and nitrates as shown in Table XXII.

In this table a tenfold height is given to the ordinates representing the nitrites, the smaller quantity in which they occur requiring this exaggeration.

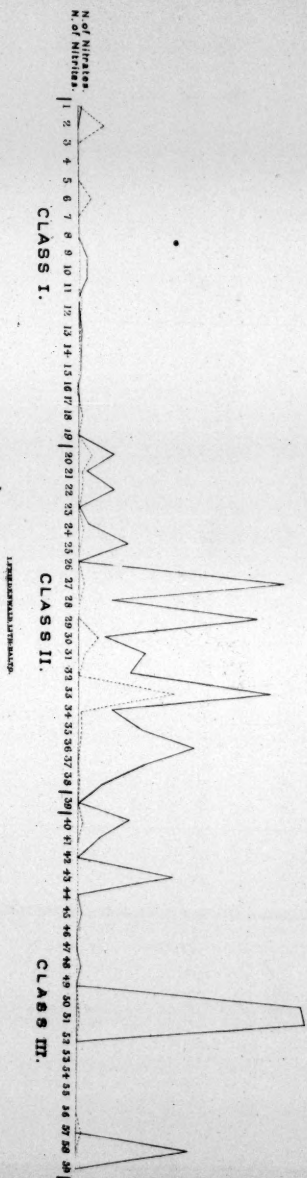
Here we find a very obvious connection between the results of chemical examination and the known sanitary character of the several waters, the salts of nitrous and nitric acid being either absent or present in but trifling amount in the waters of Class I, believed to be wholesome; almost universally present, and in many cases in large quantity, in the pernicious waters of Class II, and very variable as to presence and amount in the waters grouped together under the doubtful head of Class III. No aspect in which I have compared together the good and bad natural waters has afforded so definite a result as this.

This result is worthy of special attention in view of the different opinions which have been expressed as to the sanitary significance of nitrites and nitrates in water. Thus, Wanklyn says:<sup>2</sup> "The nitrates and nitrites have been erroneously regarded as measuring

<sup>1</sup> Tiemann and Preusse have suggested that a polluted water may more *probably* contain disease ferments than a pure one, but it should not be inferred that an impure water is necessarily pernicious. Quoted in Chem. News, January 16, 1880, 30, 31.

<sup>2</sup> J. A. Wanklyn, "Water Analysis," Lond., 1879, 97, 98.

**TABLE XXII.-Nitrites and Nitrates in natural waters examined.**



the defilement of water." "In fine, presence or abundance of nitrates does not show defilement by means of sewage, and deficiency of nitrates does not show absence of defilement. Many excellent waters have been condemned as unwholesome on account of the nitrates contained by them; and it cannot too strongly be insisted upon that the nitrates afford no data of any value in judging of the organic quality of a water." Angus Smith says:<sup>1</sup>

"There are many interesting questions to be asked regarding nitrates. I am inclined to think that their presence shows that the most dangerous state of the organic matter is past. When they appear in any solution, the chief escape of putrid gas seems to have ceased; the water may, however, be still dangerous to use, and, of course, is revolting to the imagination." . . . "Those nitrates, however, which do remain indicate that at least an equivalent of albuminous matter or sewage matter *did* exist."

Frankland clearly expresses his views<sup>2</sup> as to this evidence of "previous sewage contamination" thus:

"Large quantities [of nitrates] convict water of previous pollution by organic matters of animal origin. They tell only of the contamination which is past; but, by inference, they also declare the probable nature of the organic matter now present. . . . Whether or no the analyst should form an unfavorable opinion of the water from the amount of nitrates must depend upon the proportion of organic matter actually present, and on his confidence in the efficiency and uniform action of the purifying process."

As the basis of his determination of "previous sewage contamination" Frankland takes the sum of the nitrogen present as ammoniacal salts, nitrites, and nitrates, diminished by an allowance for the average amounts of these substances in rain-water; he therefore treats the significance of the ammonia as the same with that of the nitrites and nitrates, as evidence merely of the past presence of nitrogenous organic matter of which a part *may* remain.

Griess has expressed a strong opinion<sup>3</sup> as to the sanitary importance of detecting nitrates, and the unfitness of water for drinking purposes when containing them.

Ekin<sup>4</sup> attaches very great importance to the presence of nitrates and nitrites. Thus he says:

<sup>1</sup> Chemical News, September 3, 1869, 173.

<sup>2</sup> "Water Analysis for Sanitary Purposes," 27.

<sup>3</sup> Chemical News, June 25, 1869, 305.

<sup>4</sup> Ann. d. Chem. u. Pharm. 154, 336.

<sup>5</sup> "Potable Water," 2d ed., Lond. 1880, pp. 15, 16, 22, 25, 26, 27, 28, &c.

"Waters which have undoubtedly given rise to typhoid fever have been found by the writer over and over again not to contain more than 0.05 part of albuminoid ammonia in 1,000,000, and which, notwithstanding their containing a large excess of nitrates, have been passed by analysts of undoubted ability as being fit for drinking purposes. The attention of the writer was particularly drawn to this in the case of a district where typhoid fever was hardly ever absent, and where the conditions were such as pointed exclusively to water as being the aggravating cause. . . . Samples were taken when the pollution was evident and analyzed. Two only were found to contain an excess of albuminoid ammonia, but all contained a large excess of nitrates. . . . The significance of an excess of nitrates has already been sufficiently dwelt upon, and we have seen that both upon *a priori* grounds and as the result of actual experience, their presence in abnormal quantity is objectionable. . . . When the amount [of nitrates] exceeds 0.5 or 0.6 part [per 100,000], it points significantly to dangerous pollution; . . . nitrogen as nitrates should be invariably absent from a good water. . . . This view of the importance to be attached to an abnormal quantity of nitrates has been formed in spite of a considerable predisposition to a contrary opinion, and has been literally forced upon the writer again and again by the investigation of cases which really leave no doubt in the matter."

Reuben Haines, of Philadelphia, has furnished<sup>1</sup> the details of some cases in his own experience, which he says are "in partial corroboration of the opinions of Mr. Ekin."

Among the artificially polluted waters of the investigation now reported on, there are a number of samples of such general character as to attach to them the gravest suspicion on sanitary grounds, suspicion corroborated in sundry cases by the biological tests applied to them; in which, nevertheless, nitrates and nitrites are not found; but in these waters we find the quantity of organic matter extraordinarily large, and generally accompanied by very large amounts of ammonia—*e. g.* Nos. 119, 120, 121, containing water in which the dead body of an animal had been allowed to macerate; Nos. 122, 123, 124 containing much blood from a slaughter-house, and Nos. 137 and 138 containing the dejecta from typhoid-fever patients.

<sup>1</sup>"Methods for judging of the wholesomeness of drinking-water." From Journal of the Franklin Institute, February, 1881.



Looking at the results from the natural waters of Classes I and II, and bearing in mind the conclusions reached by Müller, Schloesing and Müntz, Storer, Warington, and others<sup>1</sup> as to the process of nitrification being due to the presence of an organized ferment or ferments of bacterial character, the idea suggests itself whether the noxious character of waters containing largely of nitrates and nitrites—themselves presumed to be harmless—and but very little organic matter—which ought to be present, of some sort, to support the "previous contamination" view—*may not be in reality due to the presence of a special nitrifying ferment, itself to be classed among the lower organisms capable of propagating disease.*

4. Two points require to be borne in mind, suggestive of caution in drawing such conclusions as the above in regard to the sanitary in connection with the chemical character of water.

In the first place the samples examined may possibly have undergone chemical change in the interval from their collection to their reaching the analysts, so that, for example, organic matter may have disappeared or nitrates may have been formed. With the precautions taken to lose as little time as possible, there does not seem much likelihood of such changes having occurred to so serious an extent as to essentially alter the character of the water.

In the second place, with the object which I had in view, of obtaining samples of water capable of producing disease, it was necessary to take what may be called *exaggerated instances* of mischief—well-marked or comparatively violent cases of illness—since no others could well be traced with sufficient strength of probability to their supposed cause, and it may very possibly be that the organic impurities present in the waters concerned in such cases are not the same as those which would produce slighter, but in time serious, ill effects. Slighter forms of disease, in reality attributable to drinking-water, may perhaps be numerous, and possibly of various types; but generally the difficulty will be too great of securing, in view of the many factors concerned, any satisfactory evidence as to their cause. The collection of strongly marked cases only, neglecting slighter ones if such exist, involves to some extent the same fault in principle as the commonly applied test of the death-rate for particular diseases in the discussion of local sanitary conditions; there may be numerous cases of illness, with but few deaths. The same difficulty also is experienced in trying

<sup>1</sup> Comptes rendus, 84, 301; 85, 22, 1018. Jour. Chem. Soc. (Lond.), January, 1878, 44; July, 1879, 429. Chem. News, November 4, 1881, 217, &c.

pathological experiments on the lower animals; only strongly marked effects can be noted or satisfactorily connected with their supposed cause.

5. In regard to the comparatively rough determinations of chlorine, the results are, in many of the cases of water from shallow wells, significant enough of contamination by fluid animal excreta. The amounts of chlorine found in specimens Nos. 2, 3 and 4 of water from the deep artesian well at Charleston, S. C., and in No. 22 from a well near the sea on Staten Island, and Nos. 50 and 51 from a well, and No. 52 from a pond in the neighborhood of the sea at Newport, R. I., illustrate the need for thought as to the natural source of a water in drawing conclusions in connection with the presence of chlorides. Even in cases in which chlorine has come in with organic matter, the impropriety of too hastily deciding, as is sometimes done, that a small quantity indicates vegetable and a large amount animal contamination, is illustrated by the results for No. 65, containing an infusion of hay or dry herbage,<sup>1</sup> and for Nos. 87 and 88, containing the alkaline washings from wood pulp at a paper-mill, in contrast with those for Nos. 120 and 121, containing a very foul infusion of the body of a dead animal, and for Nos. 138 and 139, containing morbid animal matter from cases of typhoid and scarlet fever.

*Biological results contrasted with the actual character of the waters examined.*

The lists of waters marked (independently) by Professor Martin and Dr. Hartwell as "dangerous" and "suspicious," on the basis of the biological observations, are summarized, in connection with the classes represented, in Table XXIII.

TABLE XXIII.—*Biological classification of waters.*

| Class.         | No. in class. | Professor Martin. |             | Dr. Hartwell. |             |
|----------------|---------------|-------------------|-------------|---------------|-------------|
|                |               | Dangerous.        | Suspicious. | Dangerous.    | Suspicious. |
| I . . . . .    | 19            | ...               | 4           | ...           | 7           |
| II . . . . .   | 19            | ...               | 2           | ...           | 1           |
| III . . . . .  | 20            | 2                 | 1           | 1             | 3           |
| IV . . . . .   | 20            | 3                 | 3           | 3             | 2           |
| V . . . . .    | 21            | 4                 | 5           | 2             | 10          |
| VI . . . . .   | 21            | 4                 | 1           | 1             | 6           |
| VII . . . . .  | 15            | 4                 | 3           | 4             | 7           |
| VIII . . . . . | 4             | 1                 | 2           | 2             | 1           |

<sup>1</sup> It is possible that salt may have been sprinkled over this hay in curing it, as is sometimes done, though I have no special reason to suppose so. It was upland, not salt-marsh hay.

1. It is evident on inspection of this table for Classes I to III, that, as has been remarked on a previous page, the biological methods employed will not afford the means of deciding between a wholesome and an unwholesome natural water. Several of the waters believed to be fairly wholesome for human consumption, certainly in use for drinking purposes on a large scale, are marked "suspicious," while not one of the waters believed to have proved themselves pernicious when used by man are set down as "dangerous."

2. In many cases the waters which produced most decided effects upon the rabbits contained *very large* amounts of organic matter, so large as to probably invalidate a comparison with the natural waters or with much more dilute specimens of artificial preparation.

3. On the other hand, we find in several instances, on comparing the pathological results from three different strengths of a solution of the same organic material, that it is not the strongest which has produced the most marked effects.

4. In probable support of the idea that it is not mainly the quantity of organic matter, but the presence and nature of low organisms which render drinking water unwholesome, such cases deserve attention as No. 83 in contrast with Nos. 84 and 85, and also Nos. 131, 132 and 133 (if the deaths of comparison rabbits be not considered to vitiate the results) in contrast with Nos. 134, 135 and 136. Here the pernicious character of waters containing relatively but very little organic matter seems to be distinctly indicated.

5. It is pretty plain that much difficulty in the interpretation of the biological results arises from too great differences of absolute strength in the solutions of organic matter used. In any future attempt to extend investigation in this direction it would be well to more nearly equalize the dilution, though it might perhaps prove necessary to use in all cases more organic matter than is usually found in potable water of natural origin.

*Chemical results as to animal in contrast with vegetable organic matter in water.*

1. In general the conclusions are sustained which have been usually drawn in regard to the source of organic matter, based on the more highly nitrogenous character of that from animal than that from vegetable *debris*. This remark applies to the ratio of

organic C:N obtained by the combustion process (although the value of the figures is much reduced by the errors in the method which have been pointed out), and also to the amounts of albuminoid ammonia obtained, and the consumption of oxygen from acid permanganate.

2. But the necessity for caution in drawing such conclusions, or the propriety of substituting for the statement that a given water is polluted by, say, animal matter, rather the simple assertion that the polluting material is of highly nitrogenous character, is illustrated by such cases as Nos. 89, 90, and 91, containing the alkaline washings from the manufacture of starch, and Nos. 98, 99, and 100, containing the refuse from canning tomatoes. These waters might well be supposed to be contaminated with animal matter from the evidence afforded by the chemical results, interpreted in the usual way.

3. On the other hand, the results for Nos. 104, 105, and 106, containing a watery infusion of human fæces, especially the C:N ratio, might be taken to indicate the presence of vegetable matter. This fact, well deserving attention from a sanitary point of view, is opposed to the evidence of pollution obtained where urine alone is concerned, and might modify the conclusions drawn in cases involving drainage from mixed solid and fluid excreta. The fact itself is intelligible in view of the tendency to accumulation and ultimate rejection from the intestines of the vegetable fibre<sup>1</sup> of our food and the products of its limited alteration, as well as the highly carbonaceous character of the biliary discharges.

4. The different rate of removal from water of organic carbon and organic nitrogen is in one form illustrated by the comparison of No. 119 with No. 120 and No. 121, all three containing the watery liquid in which the body of a dead animal had been macerated, as also No. 128 in contrast with Nos. 129 and 130, all containing washings from wool. The true effect of the changes taking place in the water is, however, blended with and partially obscured by the effect of difference of strength on the errors which have been pointed out belonging to determinations by the combustion process. The bearing of such changes in the C:N ratio, from both causes, on the conclusions to be drawn as to the source of pollution is very obvious.

<sup>1</sup> The infusion used was strained, but not filtered. It contained a good deal of very fine suspended material.

5. Dr. Smart, in interpreting his results by the albuminoid-ammonia process, aided, however, in some cases, by his application of the Kubel form of the permanganate process, has for most of the waters in which the organic matter was of known character (though unknown at the time to *him*) attempted to distinguish between that of vegetable and that of animal origin, and his conclusions are given in column 45 of Table X. On examining these it will be seen that in a very large proportion of cases he has been right, while some of those in which his deductions are incorrect are intelligible in the light of full consideration of all the facts. Thus, he has referred Nos. 105 and 106, containing infusion of human fæces, to the class of vegetable matter, this case having been alluded to above; and Nos. 108 and 109, containing drainings from a pile of stable manure, to the same class, this being in many respects an analogous case, and, indeed, a more strongly marked one of its kind.

*Biological results as to animal in contrast with vegetable organic matter in water.*

1. Decidedly the most noteworthy result under this head is the well-marked pathological effect produced upon rabbits by the injection of waters contaminated solely by such vegetable matter as would usually be esteemed harmless. An account has been given on previous pages of the general report of the repeated experiments with water containing an infusion of dead forest leaves (No. 68), all leading to essentially the same result. A like effect followed from the experiments with the peaty waters of the Dismal Swamp (Nos. 78 and 79).

While there have hitherto been occasional allusions by sanitary writers<sup>1</sup> to slight indisposition now and then experienced by persons drinking the peat water of mountain streams, it has been usually assumed that peaty water is *not* unwholesome, strong language on this head being often used,<sup>2</sup> and that, in general, organic matter of vegetable origin is harmless, or comparatively harmless, while that of animal origin is highly dangerous.<sup>3</sup> The results above referred to indicate that, under the special conditions of the

<sup>1</sup> Angus Smith, in Chem. News, June 25, 1869, 304. Ekin, "Potable Water," p. 15, footnote. 6th Report of Pollution of Rivers Commission, p. 34.

<sup>2</sup> Tidy, Jour. Chem. Soc. (Lond.), Jan. 1879, 65. Ekin, "Potable Water," p. 15.

<sup>3</sup> Frankland, "Water Analysis," 93-97. Tidy, Jour. Chem. Soc. (Lond.), Jan. 1879, 80-83. Ekin, "Potable Water," pp. 12, 13, 14, 15, &c. R. Haines, Methods for judging of wholesomeness of drinking waters, p. 11. De Chaumont, Arch. Ch. Pharm. XVII, 124.

experiments with rabbits, vegetable matter representing mainly or largely alteration products of woody fibre may be in a high degree pernicious.

2. It will be seen that for nearly all the waters classed as "dangerous" by Professor Martin and Dr. Hartwell the ratio of organic C : N was rather high.

3. The above conclusion as to the apparent possibility of vegetable organic matter proving itself decidedly injurious has to be qualified by observing that in the well-marked cases of such results the amount of organic matter present in the water was large, and it would not be safe to affirm on this evidence alone that similar waters, if diluted to the ordinary potable standard,<sup>1</sup> would still prove themselves capable of causing disease or death in the animals experimented on; indeed, the evidence tends rather the other way, so far as the experiments go which were made by injecting the rabbits with *the same quantities* of weaker solutions. But, on the other hand, water containing as much vegetable organic matter as No. 78 is often used for drinking purposes in peaty districts, and this very Dismal Swamp water has often been taken by choice as the supply for ships leaving port, and has been spoken of as a source of supply for the city of Norfolk; so that the discussion of wholesomeness or unwholesomeness of such water is not without practical interest.

4. If the theory be accepted, which has so much in its favor, attributing the production of disease by organic matter in drinking water not to any specifically poisonous *substance* or substances, but to the presence and action of living organisms, it seems quite conceivable that a water containing organic matter of any kind, including vegetable matter, may be harmless at one time, and harmful at another, when perhaps a different stage of fermentation or putrefactive change may have been entered upon, and special organisms may have made their appearance or entered upon a new phase of existence. Thus there might possibly be safety in drinking a peaty water, or water filtered through beds of dead forest leaves, when fresh, danger when after a certain amount of atmospheric exposure bacterial organisms had become developed, and safety again, perhaps, after the growth of such organisms had fallen off and more or less of the available organic matter had been consumed. I have been informed that old ship-captains who have often carried the water of the Dismal Swamp to sea entertain a

<sup>1</sup> See 6th Report of Pollution of Rivers Commission, p. 34.

belief that this water undergoes a "kind of fermentation," after which it becomes remarkably good and wholesome. In support of some such idea as to different stages passed through by water (containing vegetable matter) as to the development of organisms and sanitary character, leading to the possibility, on its being stored, of wholesomeness at one time and unwholesomeness at another, the microscopical and biological reports of Nos. 62, and 69, 70, and 71, are worthy of notice.

*Evidence afforded by chemical results as to putrescent or non-putrescent character of organic matter in water.*

1. Tidy has claimed<sup>1</sup> as one of the merits of the permanganate process, that it enables the distinction to be drawn between "putrescent and easily oxidizable" and "non-putrescent or less easily oxidizable" organic matter, and has given the results of some experiments to show that the former are, for the most part at any rate, disposed of within the first hour; hence his rule as to determining separately the consumption of oxygen in that time and in three hours, and comparing the results, by means of which comparison he says "we obtain data of great value by which to judge the nature of the organic impurity." In column 28 of Table X, I have given the ratio of the consumption of oxygen from permanganate used as directed by Tidy in 1 hour to that in 3 hours, the latter quantity assumed = 100. The results for those waters, the nature of the organic matter in which was known, are obviously affected variously by sundry conditions, such as the different strengths of solutions, the presence together of both easily and less easily oxidizable matter, &c., but on the whole do not afford much support to the opinion expressed by Tidy. He distinctly assumes animal matter to be, at any rate as a rule, more "putrescent and easily oxidizable" than vegetable matter, but on examining the percentages in column 28, taking the averages for the different classes of waters, we find —

|                                     | Per cent. |
|-------------------------------------|-----------|
| Organic matter of vegetable origin: |           |
| For Class IV . . . . .              | 84.0      |
| For Class V . . . . .               | 80.8      |
| Organic matter of animal origin:    |           |
| For Class VI . . . . .              | 74.5      |
| For Class VII . . . . .             | 77.6      |
| For Class VIII . . . . .            | 79.0      |



Thus, although the differences are not very great, the proportionate consumption of oxygen within the first hour is rather greater for those waters containing vegetable than for those containing animal matter. Again, judging merely by appearance, smell, &c., I should say that the waters in the foulest and most actively putrescent condition were those containing the alkaline washings from a starch factory (Nos. 89, 90, 91), the washings from the bag-filters of a sugar refinery (Nos. 92, 93, 94), the refuse from canning tomatoes (Nos. 98, 99, 100), infusion of human faecal matter (Nos. 104, 105, 106), infusion of the body of a dead animal (Nos. 119, 120, 121), mixed drainings from a slaughter-house (Nos. 125, 126, 127), and the dejecta from typhoid-fever patients (Nos. 137, 138); the average consumption of oxygen for all of these in one hour is 80 per cent. of that in three hours; almost exactly the same with the mean of all the above figures for the five classes examined (giving them equal value), viz. 79.2 per cent.

2. On the other hand, Dr. Smart has expressed the opinion, based upon his previous extensive experience with the albuminoid-ammonia process, aside from his work with it in connection with the present investigation, that *gradual* evolution of albuminoid ammonia indicates the presence of organic matter, whether of vegetable or animal origin, in a fresh, or comparatively fresh, condition, while *rapid* evolution indicates that the organic matter is in a putrescent or decomposing condition. In column 45 of Table X will be found his application of this principle of interpretation to his results obtained from the waters examined; the detailed facts as to the rate of evolution of albuminoid ammonia in the measures of distillate successively collected will be found in Appendix D. It will be seen that in a very large proportion of the cases before him Dr. Smart has interpreted correctly the general character of the water as to putrescence or comparative freshness of condition of the organic matter. Examples, however, of erroneous results from this principle of interpretation are furnished by Nos. 77, 92, 93, 94, 125, 128, and 131, nearly all of which, it may be observed, were very dilute liquids, and perhaps by the waters (Nos. 113, 114, 116, 117, and 118), containing mixed sewage from Richmond and Washington, though these, also quite dilute, can hardly be quoted as examples involving a known degree of putrescence on the part of the organic matter.

*Biological results in connection with putrescent or non-putrescent character of organic matter in water.*

On the whole, the biological results obtained, taken in connection with the history and condition of the water samples in which the nature of the organic matter was known, are in accordance with the general belief that putrescent organic matter is more dangerous than that in a fresh or but slowly decomposing condition. Taking the twenty waters which have been noticed above, as containing the most obviously foul, evil smelling, and actively putrescent material, in some of vegetable, in others of animal origin, and comparing these with the lists of waters, as classified by Professor Martin and Dr. Hartwell, we find nine classed as "dangerous," and seven as "suspicious"; of the remaining four, the fact that two represented the weakest dilutions of materials, which in stronger solutions produced marked pathological effects, deserves to be noticed.

GENERAL CONCLUSIONS, WITH A VIEW TO SANITARY APPLICATION, AS TO THE VALUE, SEPARATELY AND COLLECTIVELY, OF THE DIFFERENT PROCESSES OF WATER ANALYSIS WHICH HAVE BEEN UNDER EXAMINATION.

1. It is not possible to decide absolutely upon the wholesomeness or unwholesomeness of a drinking water by the mere use of any of the processes examined for the estimation of *organic matter*, or its constituents.

2. I would even go further, and say that, in judging the sanitary character of a water, not only must such processes be used in connection with the investigation of other evidence of a more general sort, as to the source and history of the water, but should even be deemed of secondary importance in weighing the reasons for accepting or rejecting a water not manifestly unfit for drinking on other grounds.<sup>1</sup>

3. There are no sound grounds on which to establish such general "standards of purity," as have been proposed, looking to

<sup>1</sup> It will not do merely to throw all doubts on the side of the rejection of a water, as has been more or less advocated by writers on water analysis, for there are often interests of too serious character involved in such rejection to admit of its being decided on, save upon really convincing evidence of its necessity. In view of the great and increasing difficulty of securing an adequate supply of water of satisfactory character for very large cities, is it an unpractical fancy that there may yet come to be provided a double supply through separate pipes: 1st, of water for drinking and cooking purposes only; and 2d, of water less carefully selected as to source and storage for bathing, washing, house and street cleaning, extinguishing fires, &c., the former at any rate dispersed through meters to regulate consumption?

exact amounts of organic carbon or nitrogen, "albuminoid ammonia," oxygen of permanganate consumed, &c., as permissible or not. Distinctions drawn by the application of such standards are arbitrary, and may be misleading.

4. Two entirely legitimate directions seem to be open for the useful examination by chemical means of the organic constituents of drinking water, namely, first, the detection of *very gross* pollution, such as the contamination of the water of a well by accidental bursting or crushing of soil-pipes, extensive leakage of drains,<sup>1</sup> &c., and secondly, the periodical examination of a water supply, as of a great city, in order that, the normal or usual character of the water having been previously ascertained, any suspicious changes which from time to time may occur shall be promptly detected and their cause investigated.

5. In connection with this latter application of water analysis, there seems to be no objection to the establishment of *local* "standards of purity" for drinking water, based on sufficiently thorough examination of the water supply in its usual condition.

6. With the facts of this investigation before me, I am inclined to attach special and very great importance to a careful determination of the nitrites and nitrates in water to be used for drinking.

7. If I had intrusted to me the charge of watching a large city water supply I should use all three of the principal processes for the examination of the organic matter present; each gives a certain amount of information which the others do not afford.

Under circumstances admitting only of the use of simpler means of investigation, the albuminoid ammonia and permanganate processes might be employed together, but in no case should one only of these methods be resorted to, such a course entailing practically the neglect of carbon on the one hand or nitrogen on the other.

PRACTICAL SUGGESTIONS, DRAWN FROM THE EXPERIENCE OF THE INVESTIGATION NOW REPORTED ON, AS TO THE USE IN THEIR PRESENT FORM OF THE CHEMICAL PROCESSES STUDIED.

#### *Examination of water samples in general.*

1. Great care should be taken that water samples be placed in the hands of the analyst and their examination begun with the

<sup>1</sup> Dr. J. S. Billings, U. S. A., of the National Board of Health, has suggested to me in conversation a useful subject of inquiry, viz. the possibility of tracing up the passage of polluting material through a soil by leaching samples of the soil itself, taken at various distances from the source of pollution, or from the water likely to be affected, and chemically examining the liquids obtained.

least possible delay after they have been collected. The changes which take place, sometimes rapidly, on keeping, may seriously affect the results, especially in the case of waters much polluted by foul organic matter.

2. It is very desirable that, besides examining a water in its perfectly fresh condition, samples of it should be set aside, in half-filled but closed glass-stoppered bottles, for some time—say 10 or 12 days—and one of these examined every day or two, so as to trace the character and extent of the changes undergone. Not only may conclusions be drawn from such a series of observations as to the general stability or decomposibility of the organic matter present, but light will be thrown upon the changes which may be expected to occur under ordinary conditions when the water is stored for use, as in cisterns, wells during periods of drought, or carelessly allowed to remain stagnant in pitchers, water-coolers, &c.

*Combustion process.*

1. In applying this process, no matter how skilful or well trained the analyst may be, duplicate or even triplicate concordant results should be insisted upon before accepting the determinations as trustworthy.

2. In order to avoid the presence in the atmosphere, about the water-bath used for the evaporation, of ammonia derived from coal-gas, the bath should be heated by steam brought in a small, closed pipe from a distant boiler, preferably situated in another room, and the waste steam and condensed water therefrom should be in like manner carried off to a safe distance.

*Albuminoid-ammonia process.*

1. In order to avoid the uncertain ending of the collection of ammonia, whether "free" or "albuminoid," it would be well to adopt the rule that the distillation be stopped when, and not before, the last measure of distillate collected contains less than a *certain proportion*—say 1 per cent.—of the whole quantity of ammonia already collected. This would in many cases involve the necessity of replenishing the liquid contents of the retort with ammonia-free water.

2. In order to diminish the loss of amines or other volatile forms of nitrogenous matter, a separate distillation should be made with alkaline permanganate added *at once*, in addition to the usual

course of treatment prescribed by Wanklyn—distillation begun with sodium carbonate, and continued after addition of the alkaline permanganate. The results of the two separate distillations should then be compared.

3. In reporting the results obtained by the albuminoid-ammonia process, including the determination of free ammonia, the details of the evolution of ammonia, as collected by separate measures of distillate, should always be given.

#### *Permanganate process.*

1. In view of the evidence obtained rendering probable the loss of organic matter by volatilization in the use of acidified permanganate at a boiling temperature, the Tidy form of the process is rather to be recommended than that of Kubel if but one be used.

2. On the other hand, the advantage of more extended oxidizing action, and the greater *general* accordance of the results by the Kubel process with those for organic carbon by the combustion process, make it desirable that as far as possible the same advantages should be secured by substituting the influence of time for that of temperature, and that the time during which the permanganate is allowed to act in the Tidy process should be increased to at least 12, better to 24 hours, *several* determinations (on different samples set aside at the same time) being made at such intermediate intervals as 1, 3, 6, 9, and 12 hours, in order to trace the progress of the oxidation.

#### SUGGESTIONS AS TO POSSIBLE IMPROVEMENTS ON THE PROCESSES EXAMINED DESERVING FURTHER INVESTIGATION.

##### *Combustion process.*

I would propose to evaporate the water, not under ordinary pressure and in contact with the atmosphere, as usual, but as the specimens of water were evaporated for the biological experiments, in a closed vessel immersed in a water-bath and connected with a good (water jet) air pump, so as to secure a nearly complete removal of air, with a condensing worm to dispose in part of the aqueous vapor given off. It would not do to simply place the water in a flask, since the residue could not be removed for combustion, but it would not be difficult to arrange a suitable vacuum vessel, with wide mouth and tightly clamped on cover, within

which might be placed the usual glass dish to receive the water, and the feed might be managed through a nearly capillary tube with a glass stop-cock. By such an arrangement the evaporation might be effected within a moderate time at a fixed temperature much lower than the boiling point, thus probably reducing any loss from simple volatilization of organic matter; the nearly complete exclusion of air would tend to greatly diminish or do away with loss of organic matter by oxidation, and permit of large reduction in the quantity of sulphurous acid used; for the same reason the tendency to formation of sulphuric acid would be reduced to a minimum, and the absorption of ammonia from the atmosphere about the dish would be altogether prevented. In testing this last-named effect, two bulb-tubes containing pure sulphuric acid might be interposed between the vacuum chamber and the pump; the contents of the one to be tested for ammonia given off from the water, those of the other to guard against any trace of ammonia coming back from the outside air during irregular action of the stream of water.

2. In order to avoid loss during the evaporation of readily volatile substances, such as butyric, valerianic, &c., acids, to dispense with the necessity for the uncertain and unsatisfactory correction for ammonia lost by dissociation, to get rid of the influence on the determination of organic nitrogen of any errors in the determination of the total ammonia, and to avoid corresponding difficulties arising from the presence of nitrates if these be allowed to remain, it might be well to evaporate at first with the addition of a small excess of magnesia (as recommended by Lechartier), thus removing all ammonia, and then, the water having been brought down to a small volume, add a moderate excess only of sulphurous acid<sup>1</sup> with a drop of a solution of a ferrous salt (as directed by Frankland), and complete the evaporation to dryness—the whole process to be carried out in a jet-pump vacuum, as above suggested.

3. Further experiments are desirable in order to completely determine the merits and defects of the Williams ("copper-zinc couple") method for the removal of nitrates.

4. Some preliminary experiments of my own have seemed to show that nitrates and nitrites may be completely reduced by evaporating to a small bulk with no great excess of phosphorous

<sup>1</sup> I doubt, however, the possibility of fully reducing nitrates, by means of sulphurous acid, if they are present in large quantity.

or hypo-phosphorous acid, guarding against the evolution of phosphuretted hydrogen by the low temperature employed, then adding magnesia in small excess and completing the evaporation, thus leaving the residue in a pulverulent instead of sticky condition, easy of removal from the dish, and probably allowing of complete combustion without inconvenience from the final oxidation of the small excess of phosphite or hypophosphite, and without any wrapping up of carbon particles. This plan deserves to be carefully tested.

*Albuminoid-ammonia process, including determination of free ammonia.*

1. In order to prevent, or at least to largely reduce and render uniform, the loss of ammonia from imperfect condensation, I would prefer to effect the distillation, not by a lamp-flame, but in a retort of uniformly determined shape and size, uniformly immersed in a bath of saline solution or other suitable material kept at a uniform temperature—say  $102^{\circ}$  or  $105^{\circ}$  C.—by means of steam, and to condense in a glass worm, surrounded by ice-water, sufficiently long to bring the distillate to a uniform temperature, not exceeding, say  $5^{\circ}$  C.

2. It would be perhaps still better to conduct the distillation in a completely closed apparatus, with a fixed difference of temperature between the retort and the far end of the fully effective condensing tube, with a glass stop-cock to draw off the distillate in successive measured portions, and a little safety-valve (mercury or other) near the cold end to prevent any dangerous difference of external and internal pressure.

3. In the determination of *free* ammonia, with a view to distinguishing as sharply as possible between ammonia really existing as such or in ammoniacal salts and that formed by breaking up of organic matter, it might be well to try a closed distilling apparatus connected with a (water-jet) air-pump, so as to maintain a partial vacuum within, keeping the retort at a fixed temperature much below  $100^{\circ}$  C., and collecting the whole of the ammonia in a flask and one or more bulb tubes containing rather weak mineral acid, interposed between the condenser and the pump. This would, however, be attended with the disadvantage of not readily permitting the progress of the evolution of ammonia to be traced by its collection in separate successive measures of distillate; and it would become necessary to ascertain whether the application of the



Nessler test would be in any way interfered with by the sodium salts formed from the acid used to collect the ammonia.

4. In order to overcome, if possible, the most serious difficulty in the way of a correct determination of free ammonia, namely, the ready breaking up of urea (and other amides), when present, on heating with sodium carbonate, it would be well to ascertain at how low a temperature and within what time, if at all, ammonia really existing in ammoniacal salts could be completely driven off from an *extremely dilute* solution by adding a small excess of magnesia and maintaining a (water-jet) air-pump vacuum above the liquid, forming a stratum of small depth, with bulb-tubes of acid between the liquid and the pump to intercept the ammonia, and guard-tubes to prevent any being received from the air; in other words, to ascertain whether Schlöesing's method for the determination of ammonia admits of being applied to such excessively minute amounts of it as the water analyst is concerned with.

5. In the conduct of the albuminoid-ammonia process proper, *i. e.* the distillation with alkaline permanganate, I would propose that the original volume of liquid in the retort be maintained *constant*, by running in at the proper rate, through a nearly capillary tube with a glass stop-cock, ammonia-free distilled water. And, in cases in which the amount of organic matter is so large as to wholly, or in great part, reduce the usual charge of alkaline permanganate, I would determine by a preliminary experiment at about what rate the reagent is used up, and would then progressively supply its solution, instead of simply pure water, at such a rate as to keep the original strength as nearly as possible unaltered.

#### *Permanganate process.*

1. The principle involved in the last paragraph applies also to this process. Instead of using a fixed amount of permanganate at first, and adding a second or third charge only when the former has been completely reduced, there ought to be a fixed excess at the end of the action, or rather there should be present a constant excess all through the process. Hence, when a preliminary experiment has shown that more than the usual charge of permanganate will be needed, and about the rate at which it will be consumed, for the final experiment additional permanganate solution should be gradually dripped in, from a nearly capillary tube, at such a rate as to maintain the original excess as nearly as possible constant.

2. It is desirable that the process be carried on at a pretty nearly fixed temperature.<sup>1</sup> If the Tidy method be followed, a temperature of say 20° C. could, with a little management, generally be secured, and the flasks kept approximately at this point during the time required for the action.

SUGGESTIONS AS TO FURTHER INVESTIGATIONS IN GENERAL CONNECTION WITH THE SUBJECT-MATTER OF THIS REPORT.

1. It is much to be wished that more extended biological experiments should be made upon the effects of water variously polluted on the lower animals, and that in such experiments the action of water introduced into the stomach as well as hypodermically injected should be tested, and other animals (such as dogs) used as well as rabbits.

2. It would be well to have chemical examinations, on a strictly uniform plan, from time to time made of the water supply in a few of the largest cities at periods when, not mortuary statistics, but the general assent of well-informed members of the medical profession, ascertained through local sanitary authorities, indicates unusual prevalence of, or unusual exemption from, the classes of disease most probably capable of origination from the organic pollution of drinking water.

3. I would *especially* suggest a combined chemical and biological inquiry as to the possible effects upon living animals of the ferment or ferments of nitrification in different stages of that process. In connection with this some minor questions connected with the development of nitrites and nitrates from decomposing organic matter are pointed to, by facts observed in the course of the investigation now reported on, as deserving further examination.

CONCLUSION.—ACKNOWLEDGMENT OF ASSISTANCE RECEIVED.

It remains only for me to record my thanks to the following gentlemen for aid of various kinds, obligingly rendered in connection with the work which forms the subject of this report:

To Prof. H. Newell Martin, of the Johns Hopkins University, for his kind consent to take charge of the biological part of the investigation.

<sup>1</sup> For experiments on the varying extent of action of permanganate upon organic matter in water at different temperatures, see Bericht, d. deutsch. chem. Gesellsch., 14, 1015.

To Dr. Chas. Smart, U. S. A., Dr. J. A. Tanner, U. S. N., and Mr. W. A. Noyes, Graduate Scholar of the Johns Hopkins University, for the zeal, care, and patience with which they carried out the actual chemical examination of the waters.

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## MINERALS FROM FRITZ ISLAND, PA.

BY BENJ. SADTLER, JR.

Finding that no analyses of the chabazites and mesolites of this State had been made, and having some good specimens at my command, I have analyzed both minerals. The specimens used came from Fritz Island, near Reading, Pa., where they are found associated with thomsonite, apophyllite, calcite, and, more rarely, an undescribed zeolite which has been analyzed by Dr. Genth (*Mineralogy of Penna.*, page 110.)

1. The chabazite occurs in well-developed rhombohedral crystals, rarely modified by other rhombic forms. The crystals are colorless and of a vitreous lustre, having a hardness of 4, and sp. gr. 2.3. An analysis gave the following results:

|                                |   |   |   |   |   |       |
|--------------------------------|---|---|---|---|---|-------|
| H <sub>2</sub> O               | . | . | . | . | . | 20.21 |
| SiO <sub>2</sub>               | . | . | . | . | . | 50.28 |
| Al <sub>2</sub> O <sub>3</sub> | . | . | . | . | . | 17.83 |

|                                |   |   |   |   |   |       |
|--------------------------------|---|---|---|---|---|-------|
| CaO                            | . | . | . | . | . | 6.96  |
| Na <sub>2</sub> O              | . | . | . | . | . | 2.43  |
| K <sub>2</sub> O               | . | . | . | . | . | 2.40  |
| Fe <sub>2</sub> O <sub>3</sub> | . | . | . | . | . | trace |
| MgO                            | . | . | . | . | . | .22   |

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 100.33

2. The mesolite is found in globular concretions or tufts of fine white fibres. Hardness 2.5—3, and sp. gr. 2.4. After determining and allowing for a very slight amount (about one-fifth of a per cent.) of calcite, from which it was impossible to entirely free the mineral, the analysis was as follows:

|                                |   |   |   |   |   |       |
|--------------------------------|---|---|---|---|---|-------|
| H <sub>2</sub> O               | . | . | . | . | . | 16.01 |
| SiO <sub>2</sub>               | . | . | . | . | . | 43.29 |
| Fe <sub>2</sub> O <sub>3</sub> | . | . | . | . | . | trace |
| Al <sub>2</sub> O <sub>3</sub> | . | . | . | . | . | 25.02 |
| CaO                            | . | . | . | . | . | 12.15 |
| Na <sub>2</sub> O              | . | . | . | . | . | 3.40  |

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 99.87

3. I also made an analysis of the apophyllite from the same locality. It occurred in tetragonal tablets modified by octahedral planes. The crystals were colorless and of a pearly lustre. Hardness 4—4.5, sp. gr. 2.5. Appended is the analysis:

|                                |   |   |   |   |   |       |
|--------------------------------|---|---|---|---|---|-------|
| H <sub>2</sub> O               | . | . | . | . | . | 16.75 |
| SiO <sub>2</sub>               | . | . | . | . | . | 51.02 |
| Fe <sub>2</sub> O <sub>3</sub> | . | . | . | . | . | 1.49  |
| CaO                            | . | . | . | . | . | 24.40 |
| K <sub>2</sub> O               | . | . | . | . | . | 5.87  |
| Fl                             | . | . | . | . | . | .40   |

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 99.93

## MANGANESE BORATE.

BY N. WILEY THOMAS.

In a recent article<sup>1</sup> published by Smith, upon the determination of boracic acid, a precipitate was obtained to which the formula  $\text{MnB}_4\text{O}_7$  was assigned. I have since been requested to examine this compound, and append my results.

The salt was obtained by precipitating 10 cc. borax solution (containing .1000 gram  $\text{Na}_2\text{B}_4\text{O}_7 + 10\text{H}_2\text{O}$ ) with 10 cc. manganese sulphate (.0600 gram  $\text{MnSO}_4$ ) in presence of alcohol. After the precipitate had completely subsided, it was rapidly filtered and washed with alcohol. The alcoholic filtrate was evaporated, and the excess of manganese sulphate determined with a solution of potassium permanganate, 1 cc. of which = .0045 gram  $\text{MnSO}_4$ . The excess required 4.6 cc.  $\text{KMnO}_4$ , corresponding to .0207 gram  $\text{MnSO}_4$ .

The manganese borate after washing was dissolved in sulphuric acid and evaporated to dryness several times, the residual manganese sulphate dissolved in water, zinc sulphate added, heat applied, and potassium permanganate run in until a permanent pink color was imparted to the liquid. The  $\text{KMnO}_4$  used was 8.6 cc., corresponding to .0387 gram  $\text{MnSO}_4 = .0180$  gram  $\text{MnO}$ . The 10 cc. manganese sulphate contained .0600 gram. The excess of  $\text{MnSO}_4$  in the filtrate determined by  $\text{KMnO}_4 = .0207$ . The quantity of manganese sulphate then reacting with 10 cc.  $\text{Na}_2\text{B}_4\text{O}_7 = .0600 - .0207$  or .0393  $\text{MnSO}_4$ , and by actual determination I found .0387 gram.

$$.0393 \text{ gram } \text{MnSO}_4 = .0183 \text{ gram } \text{MnO}.$$

$$.0387 \quad " \quad " \quad = .0180 \quad " \quad "$$

In the borax solution (0.1000 gram borax) there is .0366 gram boron trioxide, and this would require .0183 gram  $\text{MnO}$  for union. As already noticed above, I found by actual determination .0180 gram  $\text{MnO}$  in the borate. Upon comparing the amounts of boron trioxide and manganous oxide found, we have:

<sup>1</sup> This Journal 4, 279.

$$\begin{array}{rcl} .0180 \text{ gram MnO} \div 70 & = & 25 \div 25 = 1 \text{ mol. MnO} \\ .0366 \text{ " " " } \div 70 & = & 50 \div 25 = 2 \text{ mol. B}_2\text{O}_3 \end{array}$$

or the formula would be  $\text{MnB}_4\text{O}_7$ , as written.

A second determination gave the following:

In this case the salt was obtained by precipitating 5 cc. borax solution (same strength as preceding) with 5 cc. manganese sulphate (also previous strength) in the presence of alcohol. The operation was carried out as in the first case. The required  $\text{KMnO}_4$  was 4.3 cc., corresponding to .0194 gram  $\text{MnSO}_4 = .0090$   $\text{MnO}$ . The 5 cc. manganese sulphate contained .0300 gram. The excess of  $\text{MnSO}_4$  in the filtrate determined by  $\text{KMnO}_4 = .0104$  gram. The quantity of manganese sulphate then reacting with the 5 cc. borax solution equalled  $.0300 - .0104 = .0196$  gram. By analysis I found .0193 gram. These results lead to the same formula for the borate as those above.

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## DETERMINATION OF IRON IN HYDROCHLORIC ACID SOLUTIONS BY POTASSIUM PERMANGANATE.

BY N. WILEY THOMAS.

Zimmerman has described<sup>1</sup> a modification of Margueritte's method for determining iron in presence of hydrochloric acid, and finds that manganous sulphate prevents the chlorine from acting upon the permanganate, while nickel, cobalt and copper salts are worthless. It appears not amiss to mention that in this laboratory we have employed a solution of lead chloride for the same purpose that Zimmerman uses manganous sulphate, and find upon comparing results with those in which the manganese salt has been used, that they agree remarkably well. As they may be of interest to chemists I record them here, and also give analyses in which only sulphuric acid was present, with several in which manganous sulphate was employed.

The solutions used were of the following concentrations:  $\text{MnSO}_4 = 100$  grams in 200 cc.  $\text{H}_2\text{O}$ ,  $\text{HCl} = 1.1398$  sp. gr. and 1.20,  $\text{PbCl}_2$ ,

<sup>1</sup> *Annalen der Chemie*, 213, 307.



= 5 grams in 100 cc.  $H_2O$ . 1 cc. of the  $KMnO_4$  solution equalled .00528 gram metallic Fe.

| Iron Solution.<br>cc. | $H_2O$ .<br>cc. | HCl.<br>cc. | $PbCl_2$ .<br>cc. | $MnSO_4$ .<br>cc. | $H_2SO_4$ .<br>cc. | $KMnO_4$ .<br>cc. |
|-----------------------|-----------------|-------------|-------------------|-------------------|--------------------|-------------------|
| 1.....50              | 300             | ...         | ...               | ...               | 20                 | 27.6              |
| 2.....50              | 300             | ...         | ...               | ...               | 20                 | 27.6              |
| 3.....50              | 300             | 35          | ...               | 10                | ...                | 27.6              |
| 4.....50              | 300             | 20          | ...               | 10                | ...                | 27.6              |
| 5.....50              | 400             | 35          | ...               | 10                | ...                | 27.6              |
| 6.....50              | 400             | 20          | 10                | ...               | ...                | 27.6              |
| 7.....50              | 400             | 30          | 10                | ...               | ...                | 27.6              |
| 8.....50              | 400             | 20          | 10                | ...               | ...                | 27.6              |
| 9. ....50             | 400             | 20          | 10                | ...               | ...                | 27.6              |
| 10.....50             | 400             | 20          | 10                | ...               | ...                | 27.6              |
| 11.....50             | 400             | 20          | 10                | ...               | ...                | 27.6              |
| 12.....50             | 400             | 20          | 10                | ...               | ...                | 27.6              |

MUHLENBERG COLLEGE, ALLENTOWN, PA., NOV. 11, 1882.

Contributions from the Chemical Laboratory of Harvard College.

## XXVII.—ON CERTAIN SUBSTANCES OBTAINED FROM TURMERIC.—CURCUMIN.<sup>1</sup>

By C. LORING JACKSON AND A. E. MENKE.

The following paper<sup>2</sup> contains a description of our experiments on the action of nascent hydrogen and of bromine upon curcumin.

### *Action of Nascent Hydrogen.*

*Dihydride of Curcumin*,  $C_{14}H_{16}O_4$ .—This substance was made by the action of sodium amalgam and water upon curcumin. The best result was obtained when a mixture of curcumin, dilute alcohol, and strong sodium amalgam was allowed to stand for somewhat more than a week. The alcohol, though not absolutely necessary, as the sodic hydrate formed gradually brings the curcumin into

<sup>1</sup> From the Proceedings of the American Academy of Arts and Sciences. Communicated by the authors.

<sup>2</sup> The first paper was published in this Journal 4, 77.

solution, accelerates the action, which at best is extremely slow. After the dark-red color of the sodic salt of curcumin had given place to a blackish tinge, the liquid was poured off from the mercury, acidified with hydrochloric acid, the fawn-colored precipitate thus obtained washed till free from acid, and dried *in vacuo*. A combustion gave the following results:

0.2290 gram of substance gave 0.5678 gram of  $\text{CO}_2$  and 0.1312 gram of  $\text{H}_2\text{O}$ .

|          | Calculated for $\text{C}_{14}\text{H}_{16}\text{O}_4$ . | Found. |
|----------|---------------------------------------------------------|--------|
| Carbon   | 67.74                                                   | 67.63  |
| Hydrogen | 6.49                                                    | 6.36   |

*Properties.*—It forms a brownish-white powder melting in the neighborhood of  $100^\circ$ , but with no definite melting point; it is insoluble in water, freely soluble in alcohol and glacial acetic acid, slightly in ether, and insoluble in ligroine and benzol. Strong sulphuric acid dissolves it with a reddish-brown color, very different from the purple produced by curcumin. Sodic hydrate dissolves it on warming, and so does sodic carbonate; but the latter solution becomes turbid, and throws down a brownish precipitate on cooling.

The addition of hydrogen to curcumin by sodium amalgam and dilute alcohol is a tedious process, occupying more than a week and giving a very bad yield, the product being frequently accompanied by a viscous substance, probably formed by the action of air on the alkaline solution of the hydride. A much better method of adding hydrogen to curcumin consisted in treating it with zinc dust and acetic acid, although in this case the hydride at first produced was further modified in the course of the reaction.

*Anhydride of Curcumin Dihydride,  $(\text{C}_{14}\text{H}_{16}\text{O}_4)_2\text{O}$ .*—Curcumin was warmed with acetic acid of 85 per cent. and a large quantity of zinc dust, the temperature being kept below the boiling point of the acetic acid. After some hours the yellow color of the solution had become replaced by a dark brown, and if then a little of the substance gave a yellow instead of a red color with sodic hydrate, the heating was discontinued, and the liquid filtered into water, which precipitated fawn-colored flocks similar to those of the preceding compound. After we had satisfied ourselves that it was impossible to crystallize the substance, we purified it by resolution in glacial acetic acid and precipitation with water; but even this treatment did not remove the whole of the zinc salt, as was shown by the appearance of a slight ash on combustion. This has been

subtracted from the weight of the substance taken in calculating the percentages.

The same substance was obtained when curcumin was heated with zinc dust and a solution of ammoniac hydrate. The combustion marked III was of a product made in this way:

The substance after thorough washing with water was in each case dried on a steam radiator at a temperature of about 60°.

I. 0.2552 gram of substance gave 0.6460 gram of  $\text{CO}_2$ . 0.1476 gram of  $\text{H}_2\text{O}$ . Ash = 0.004.

II. 0.2449 gram of substance gave 0.6183 gram of  $\text{CO}_2$ . 0.1368 gram of  $\text{H}_2\text{O}$ . Ash = 0.0061.

III. 0.2357 gram of substance gave 0.6001 gram of  $\text{CO}_2$ . 0.1365 gram of  $\text{H}_2\text{O}$ . Ash = 0.002.

| Calculated for $\text{C}_{28}\text{H}_{30}\text{O}_7$ . |       | Found.             |                    |                    |
|---------------------------------------------------------|-------|--------------------|--------------------|--------------------|
|                                                         |       | I.                 | II.                | III.               |
| Carbon                                                  | 70.42 | 70.14 <sup>1</sup> | 70.61 <sup>1</sup> | 70.03 <sup>1</sup> |
| Hydrogen                                                | 6.25  | 6.53               | 6.36               | 6.48               |

*Properties.*—It resembles the dihydride closely, like it forming a dirty white powder, with no definite melting point, since it melts gradually in the neighborhood of 120°. The best solvents for it are alcohol and glacial acetic acid, but it is deposited on evaporation of the solvent as a varnish. It is essentially insoluble in ether, ligroine, and benzol, slightly soluble in chloroform. A solution of potassic hydrate dissolves it with a yellow color, while potassic carbonate forms a dark-brown solution if boiled with it, but as this solution cools, brownish flocks are deposited, which we supposed to be a potassium salt, until two analyses of the substance showed that it did not contain more than 2.5 per cent. of potassium, whereas the salt with the least possible amount of the metal contains 7.5 per cent. It is evident, therefore, that the potassium was an impurity, which could well be, since we were able to find no satisfactory method of purification. An attempt to make a potassium salt with alcoholic potassic hydrate gave a black liquid, insoluble in a mixture of alcohol and ether, and of the most unpromising appearance.

<sup>1</sup> If the ash is not subtracted the percentages are—

| I.    | II.   | III.  |
|-------|-------|-------|
| 69.04 | 68.85 | 60.44 |
| 6.43  | 6.20  | 6.43  |

The fact that the substance forms no salt with potassic carbonate indicates that the two molecules of the dihydride are connected by the removal of water from their carboxyl groups; but we did not consider the nature of the substance satisfactorily explained until we succeeded in making it from the dihydride,  $C_{14}H_{16}O_4$ , by the action of an acetic acid solution of zinc acetate. After warming the two substances together for some time, the product was treated with water, and the precipitate washed, dried, and analyzed, with the following result:

0.1430 gram of substance gave 0.3666 gram of  $CO_2$  and 0.0868 gram  $H_2O$ .

|          | Calculated for $C_{28}H_{30}O_7$ . | Found. |
|----------|------------------------------------|--------|
| Carbon   | 70.42                              | 69.92  |
| Hydrogen | 6.25                               | 6.68   |

Whereas before this treatment a portion of the same sample gave carbon 67.63, hydrogen 6.36, as on page 361. This experiment proves, therefore, that the nascent hydrogen given off by zinc dust and acetic acid first converts the curcumin into the dihydride, from which the zinc acetate afterward removes one molecule of water. The anhydride is broken up only incompletely by the action of water at high temperatures or by boiling with sodic hydrate, the product in each case being a mixture of the dihydride and its anhydride.

In order to study the oxidation of the dihydride, some diethyl-curcumin, prepared according to the method given in our first paper, was treated with zinc dust and acetic acid. The product thus obtained gave the following results on analysis, which indicate that it is a mixture of di- and monoethyl-curcumin dihydride:

I. 0.2130 gram of substance gave 0.5484 gram of  $CO_2$  and 0.1415 gram of  $H_2O$ . Ash 0.0004.

II. 0.1938 gram of substance gave 0.4986 gram of  $CO_2$  and 0.1336 gram of  $H_2O$ .

|          | Calculated for<br>$(C_2H_5)_2C_{14}H_{16}O_4$ . | I.    | Found. | II.   | Calculated for<br>$(C_2H_5)_2C_{14}H_{16}O_4$ . |
|----------|-------------------------------------------------|-------|--------|-------|-------------------------------------------------|
| Carbon   | 69.59                                           | 70.35 |        | 70.15 | 71.05                                           |
| Hydrogen | 7.25                                            | 7.40  |        | 7.66  | 7.89                                            |

Some of this substance was mixed with a saturated neutral solution of potassic permanganate and allowed to stand at the ordinary temperature. The oxidation took place very slowly, several weeks'

standing being necessary to complete the reaction. The principal product was proved by its melting point to be ethylvanillic acid, while the presence of a small quantity of ethylvanillin was indicated by its characteristic smell.

The most striking fact in connection with this reaction was that the dihydride was oxidized with much more difficulty than curcumin itself.

*Action of Bromine on the Anhydride of Curcumin Dihydride.* When the hydride, dissolved in glacial acetic acid, was mixed with an excess of bromine and allowed to stand over night, the liquid turned black, and upon addition of water, a red precipitate was thrown down, which was washed with water, dried, and analyzed:

I. 0.6652 gram of substance gave 0.7160 gram of  $\text{CO}_2$  and 0.1122 gram of  $\text{H}_2\text{O}$ . 0.3100 gram gave according to Carius 0.4125 gram of AgBr.

II. 0.3202 gram gave 0.3498 gram of  $\text{CO}_2$  and 0.0562 gram of  $\text{H}_2\text{O}$ . 0.2786 gram gave 0.3730 gram of AgBr.

| Calculated for $\text{C}_{14}\text{H}_{10}\text{Br}_4\text{O}_4$ . |       | Found. |       |
|--------------------------------------------------------------------|-------|--------|-------|
|                                                                    |       | I.     | II.   |
| Carbon                                                             | 29.89 | 29.36  | 29.80 |
| Hydrogen                                                           | 1.78  | 1.87   | 1.95  |
| Bromine                                                            | 56.94 | 56.62  | 56.99 |

The substance is red and amorphous; it does not melt under a red heat, but seems to be decomposed without melting. It is insoluble in water, ligroine, and benzol, very slightly soluble in alcohol and ether, soluble in glacial acetic acid. Strong sulphuric acid has no action upon it. It is vigorously acted on by boiling potassic hydrate, forming a red solution, from which acids precipitate a black tarry body which we were unable to purify; two analyses of its sodium salt, however, showed that it contained about the same percentage of oxygen as of carbon, and that most of the bromine (all but 7 per cent.) had been removed, proving that the bromine in the original substance is all in the side-chain.

#### *Action of Bromine on Curcumin.*

We have obtained two bromine compounds of curcumin, one containing four and the other seven atoms of bromine.

*Tetrabromide of Curcumin*,  $\text{C}_{14}\text{H}_{14}\text{Br}_4\text{O}_4$ .—When curcumin suspended in carbonic disulphide is allowed to stand with an excess of bromine for some hours, it is converted into a white sub-

stance, which is left as the carbonic disulphide evaporates. The carbonic disulphide can be replaced by glacial acetic acid, but in this case an excess of bromine or the use of a large quantity of glacial acetic acid must be avoided. The nature of this body could not be established satisfactorily by analysis, as it was more or less decomposed by all its solvents, and therefore a thorough purification was impossible; we have obtained one fair analysis, however, of a sample washed with carbonic disulphide.

0.2375 gram of substance gave according to Carius 0.3180 gram of AgBr.

|         | Calculated for $C_{14}H_{14}Br_4O_4$ . | Found. |
|---------|----------------------------------------|--------|
| Bromine | 56.66                                  | 56.99  |

Other specimens contained the following percentages :

|         |       |       |       |
|---------|-------|-------|-------|
| Bromine | 54.87 | 58.51 | 58.57 |
|---------|-------|-------|-------|

To confirm this result, which points to the taking up of four atoms of bromine, we determined the increase of weight caused by the bromine. For this purpose carbonic disulphide and bromine in excess were added to a weighed amount of curcumin, and the product weighed after drying it a little below  $100^\circ$ .

I. 0.252 gram of curcumin gained 0.354 gram.

II. 0.218 gram gained 0.300 gram.

These results correspond to the following percentages of bromine in the product,—

|         | Calculated for $C_{14}H_{14}Br_4O_4$ . | I.    | Found. | II.   |
|---------|----------------------------------------|-------|--------|-------|
| Bromine | 56.66                                  | 58.41 |        | 57.91 |

And there is therefore no doubt that the substance contains four atoms of bromine. To decide whether it was an addition or substitution product, we determined the amount of hydrobromic acid given off, as in every preparation an evolution of this gas was observed. For this purpose the gases formed in the reaction were allowed to pass through water, and finally the carbonic disulphide and excess of bromine were removed, at first from the curcumin, and afterward from the absorbing water, by a stream of air; the hydrobromic acid collected in the water was then determined as argentic bromide. One gram of curcumin was used in each case, and in the following comparison of results the amounts found

are compared with the calculated amount if the curcumin had given off two molecules of hydrobromic acid,—

|                    |       |      |
|--------------------|-------|------|
| Two Molecules HBr. | I.    | II.  |
| 0.66               | 0.185 | 0.28 |

From this it appears that the hydrobromic acid is produced by an insignificant secondary reaction, and that the substance is an addition product, and therefore has the formula  $C_{14}H_{14}Br_2O_4$ .<sup>1</sup> We may add that some experiments to determine directly the number of molecules of bromine added pointed to two molecules as the probable amount, but the results are not definite enough to make them worth publishing.

*Properties.*—It is a white or whitish amorphous substance, melting in the neighborhood of  $185^\circ$  with decomposition, but it has no definite melting point. It is insoluble in water, soluble with decomposition in alcohol and in glacial acetic acid, which acts upon it, however, less rapidly than the alcohol, very slightly soluble in ether, chloroform, and carbonic disulphide, insoluble in ligroïne and benzol. Its behavior with various reagents was taken up, but no results were obtained which promised to repay further study. The following observations, however, are of some interest. Potassic hydrate and also argentic oxide convert it in part into vanillin, to judge from the smell, while both anilin and zinc cleaned with sulphuric acid act upon it, the former with considerable evolution of heat,—thus confirming the inference that it is an addition product. The principal products from these reactions, as well as those from the action of sodic carbonate and water, and of reducing agents, are ill-defined bodies which we could find no means of purifying.

*Pentabromcurcumin dibromide*,  $C_{14}H_2Br_7O_4$ .—If curcumin in glacial acetic acid is treated with an excess of bromine, or the solid tetrabromide treated with bromine, a red substance is formed, which, after washing with water and drying *in vacuo*, gave the following results:

0.2898 gram of substance gave 0.2230 gram of  $CO_2$  and 0.0304 gram of  $H_2O$ .

0.2666 gram of substance gave according to Carius 0.9323 gram of AgBr.

|          | Calculated for $C_{14}H_2Br_7O_4$ . | Found. |
|----------|-------------------------------------|--------|
| Carbon   | 20.97                               | 20.98  |
| Hydrogen | 1.12                                | 1.16   |
| Bromine  | 69.91                               | 69.02  |

<sup>1</sup> The high percentages of bromine obtained in the analyses may be accounted for by this secondary reaction.



*Properties.*—A red amorphous substance melting near  $120^{\circ}$ , but without definite melting point; insoluble in water, soluble in alcohol apparently with decomposition, easily soluble in ether and glacial acetic acid, leaving a varnish, slightly soluble in benzol, insoluble in ligroine. Strong sulphuric acid acts on it very slowly, finally turning it a more brilliant red. Our study of the behavior of this substance has led to no more definite results than in the case of the tetrabromide.

Heated alone, it gives off bromine and hydrobromic acid, leaving a black tar, from which a yellow substance containing bromine can be extracted by alcohol; we may study this experiment more carefully hereafter. Sodid hydrate, sodic carbonate and water, sodic alcoholate, and argentic oxide all act upon it, but no smell of vanillin was observed in any case. The same is true of several oxidation experiments we have tried upon it, and this would seem to indicate the presence of a portion of the bromine in the benzol ring. It is an interesting fact that potassic dichromate and sulphuric acid, and also neutral potassic permanganate, attack this substance only with extreme difficulty, whereas they both act vigorously on curcumin.

#### SUMMARY.

1. Curcumin takes up two atoms of hydrogen when treated with nascent hydrogen.

2. The dihydride thus formed passes over easily into an anhydride by losing one molecule of water.

3. The anhydride of diethylcurcumin dihydride is much less easily attacked by oxidizing agents than diethylcurcumin, but the products are the same,—ethylvanillic acid with a trace of ethylvanillin.

4. Bromine removes two atoms of hydrogen from the dihydride, and replaces four more, forming  $C_{14}H_{10}Br_4O_4$ .

5. Only four atoms of bromine can be added to curcumin.

6. The tetrabromide has a great tendency to form vanillin when treated with substances which remove bromine.

7. With an excess of bromine a substance,  $C_{14}H_8Br_7O_4$ , is formed.

8. The pentabromcurcumindibromide is oxidized in neutral or acid solutions only with great difficulty.

The observations just described throw some light upon the nature of the side-chain of curcumin, but as the inferences to be

drawn from them are at best extremely doubtful, we shall postpone all discussion of the structure of curcumin until our further study of it has put the subject on a more secure basis.

## XXVIII.—TURMERIC OIL.—TURMEROL.

— BY C. LORING JACKSON AND A. E. MENKE.

The oil obtained from turmeric, which amounts to about 11 per cent. of its whole weight, has naturally attracted the attention of chemists much less than curcumin, the yellow coloring-matter of the root; we find consequently only a few analyses and some meagre statements about the action of reagents upon the oil, in place of the much fuller study to which curcumin had been submitted. The most important of these will be found in the papers of Ivanow-Gajewsky<sup>1</sup> and Kachler,<sup>2</sup> but as they all refer to mixtures, it is not necessary to repeat them here. The oil, however, is not without practical interest, as to it the turmeric (and therefore curry powder) owes its aromatic taste and smell.

The crude product with which we started in the following study of the oil was extracted from ground Bengal tumeric with ligroine, in the way already described in the first paper<sup>3</sup> of this series. After being freed from the higher boiling portions of the ligroine by heating to 150° in a boiling flask, it formed a rather thick oily liquid, with a yellow color and pleasant aromatic smell. The purification offered some difficulty, because it was decomposed by distillation under ordinary pressure, giving distillates with a rank, disagreeable smell; and distillation with steam, although effecting a partial purification, was an extremely tedious process, owing to the difficulty with which the oil was driven over. We were therefore obliged to resort to fractional distillation under diminished pressure, and in this way at last succeeded in separating the oil into three fractions—the first, boiling below 193° under 60 mm. of pressure; the second, from 193°–198°; and the third, the retort residue, a viscous, semi-solid body of extremely uninviting appearance. We have up to this time confined our attention to the middle fraction, although a

<sup>1</sup> *Berichte der deutschen chemischen Gesellschaft*, **172**, 1103.

<sup>2</sup> *This Journal*, **4**, 77.

<sup>3</sup> *Ibid.* **170**, 713.

few experiments on the fraction below  $193^{\circ}$  would indicate that it consists of the middle fraction contaminated with hydrocarbons from the ligroine used in the extraction of the oil—a view which is borne out by the very small amount of this fraction. For the fraction from  $193^{\circ}$ – $198^{\circ}$ , which is the subject of this paper, we would propose the name *turmerol*.

#### Composition of Turmerol.

I. 0.1924 gram of the oil gave 0.5903 gram of  $\text{CO}_2$  and 0.1814 gram of  $\text{H}_2\text{O}$ .

II. 0.3126 gram gave 0.9588 gram of  $\text{CO}_2$  and 0.3010 gram of  $\text{H}_2\text{O}$ .

III. 0.2354 gram gave 0.7157 gram of  $\text{CO}_2$  and 0.2190 gram of  $\text{H}_2\text{O}$ .

IV. 0.2002 gram gave 0.6123 gram of  $\text{CO}_2$  and 0.1818 gram of  $\text{H}_2\text{O}$ .

V. 0.2448 gram gave 0.7492 gram of  $\text{CO}_2$  and 0.2306 gram of  $\text{H}_2\text{O}$ .

|          | I.    | II.   | III.  | IV.   | V.    | Mean. |
|----------|-------|-------|-------|-------|-------|-------|
| Carbon   | 83.68 | 83.66 | 82.90 | 83.43 | 83.47 | 83.62 |
| Hydrogen | 10.47 | 10.70 | 10.34 | 10.10 | 10.47 | 10.42 |

I–III are analyses of the same sample; IV and V analyses of a different sample. To test the purity of the oil, the original sample was distilled again *in vacuo*, and collected in three equal fractions. Of the analyses which follow, VI was made with the portion which came over first; VII and VIII with that which came over last.

VI. 0.3315 gram gave 1.0194 gram of  $\text{CO}_2$  and 0.3145 gram of  $\text{H}_2\text{O}$ .

VII. 0.2837 gram gave 0.8675 gram of  $\text{CO}_2$  and 0.2604 gram of  $\text{H}_2\text{O}$ .

VIII. 0.2706 gram gave 0.8228 gram of  $\text{CO}_2$  and 0.2474 gram of  $\text{H}_2\text{O}$ .

|          | Lower Fraction.<br>VI. | Higher Fractions.<br>VII.      VIII. |       |
|----------|------------------------|--------------------------------------|-------|
| Carbon   | 83.86                  | 83.39                                | 82.92 |
| Hydrogen | 10.54                  | 10.20                                | 10.16 |

From this it appears that the substance is essentially pure and homogeneous.

As has been stated already, the turmerol can be purified to a certain extent by distillation with steam; analysis IX was made with a sample prepared in this way, while X was made with some of the same sample after it had been distilled once under ordinary pressure. These specimens were extracted with carbonic disulphide instead of ligroine.

IX. 0.2260 gram gave 0.6860 gram of  $\text{CO}_2$  and 0.2195 gram of  $\text{H}_2\text{O}$ .

X. 0.2636 gram gave 0.8038 gram of  $\text{CO}_2$  and 0.2546 gram of  $\text{H}_2\text{O}$ .

|          | IX.   | X.    |
|----------|-------|-------|
| Carbon   | 82.78 | 83.16 |
| Hydrogen | 10.77 | 10.73 |

The analyses unfortunately are not capable of establishing the formula of turmerol with certainty, since the difference between the members of the homologous series is very small, as is shown by the following comparison:

|          | Mean of the<br>Preceding Analyses. | $\text{C}_{18}\text{H}_{26}\text{O}$ . | $\text{C}_{19}\text{H}_{28}\text{O}$ . | $\text{C}_{20}\text{H}_{30}\text{O}$ . |
|----------|------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------|
| Carbon   | 83.62                              | 83.73                                  | 83.81                                  | 83.90                                  |
| Hydrogen | 10.42                              | 10.08                                  | 10.29                                  | 10.49                                  |

Taking both the hydrogen and the carbon into consideration, our results agree best with the formula  $\text{C}_{19}\text{H}_{28}\text{O}$ , as shown above in the case of the mean, and a comparison of the separate analyses with the calculated percentages also declares in favor of this formula. But it is evident that it is impossible to decide definitely from these data in favor of this formula, nor can the derivatives we have prepared from the oil settle this question, as a thorough purification of these bodies has proved impossible on account of their ill-defined properties and slight stability.

We are inclined to ascribe the difference between analyses VI and VII and VIII to the presence of a trace of some hydrocarbon from the ligroine, but did not attempt to purify the substance further, as it is slightly decomposed, even by distillation, under a pressure of 60 mm.

#### *Properties of Turmerol.*

The substance analyzed by us had a pale yellow color, an agreeable, not very strong aromatic smell, and a specific gravity of

0.9016 at 17°. It turns a ray of polarized light to the right with the following specific rotary power for sodium light :

$$[\alpha] = 33.52.$$

Under ordinary pressure it boils at 285°–290°, but decomposes apparently with formation of water, giving a substance with a lower boiling point. At a pressure of 60 mm. it boils from 193°–198°, but even under this pressure suffers a slight decomposition. It is essentially insoluble in water, but mixes easily with all other common solvents. Acid sodic sulphite in aqueous solution has no action upon it.

In order to determine the nature of turmerol, its behavior with various reagents was next studied.

*Action of Hydrochloric Acid.—Turmerylchloride.*

When turmerol was heated with aqueous hydrochloric acid saturated at 0° to 150° in a sealed tube for some hours, a brown oily liquid was formed having a different smell from the original substance, which, when washed until free from acid and dried *in vacuo*, gave the following results on analysis :

I. 0.2938 gram of substance gave 0.8464 gram of CO<sub>2</sub> and 0.2530 gram of H<sub>2</sub>O.

0.4434 gram of substance gave according to Carius 0.2190 gram of AgCl.

II. 0.3179 gram of substance gave 0.1518 gram of AgCl.

| Calculated for C <sub>19</sub> H <sub>27</sub> Cl. |              | Found.       |       |
|----------------------------------------------------|--------------|--------------|-------|
|                                                    |              | I.           | II.   |
| Carbon                                             | 78.48        | 78.57        |       |
| Hydrogen                                           | 9.30         | 9.57         |       |
| Chloride                                           | 12.22        | 12.21        | 11.80 |
|                                                    | <hr/> 100.00 | <hr/> 100.35 |       |

Analyses I and II were made with specimens from different preparations. The substance was a pale brownish oil with an agreeable smell, different from that of turmerol; it decomposed on distillation, and also lost chlorine when distilled with steam or even with fuming hydrochloric acid.

The same compound was formed by the action of phosphorous trichloride on turmerol, but much less neatly. Phosphoric pentachloride, on the other hand, seemed to add chlorine also, as the

product from its action on turmerol contained about 15 per cent. of chlorine. We have postponed the study of this substance for the present.

The formation of the turmerylchloride described above indicates that turmerol is an alcohol, and to confirm this view we next treated the turmerylchloride with various reagents, and found that its chlorine was removed, in part, at least, by boiling water or by alcoholic solutions of sodic acetate, potassic cyanide, or ammonia—a substance being formed in each case with the characteristic smell of the class to which it should belong. The regenerated alcohol and the acetate we were unable to purify, while the nitrile and its corresponding acid and the amine were formed in very small quantities and did not give crystalline compounds, so that their further study, which we had at first hoped would establish the formula of turmerol, did not promise to repay the labor.

To still further confirm the alcoholic nature of turmerol, we prepared the sodium compound as follows:

#### *Action of Sodium on Turmerol.*

Some of the turmerol mixed with high boiling ligroine was warmed with sodium in a flask with a return cooler for twelve hours, during which time hydrogen was given off; the liquid was then filtered, and the ligroine evaporated off from the viscous filtrate.

I. 0.1456 gram of substance gave 0.0374 gram of  $\text{Na}_2\text{SO}_4$ .

II. 0.9820 gram gave 0.2342 gram of  $\text{Na}_2\text{SO}_4$ .

| Calculated for $\text{C}_{10}\text{H}_{27}\text{ONa}$ . |      | Found. |      |
|---------------------------------------------------------|------|--------|------|
|                                                         |      | I.     | II.  |
| Sodium                                                  | 7.82 | 8.32   | 7.72 |

The substance forms a viscous semi-solid mass.

Sodic hydrate seemed not to act upon turmerol.

An attempt to convert turmerol into its acetate by heating it with acetic anhydride and sodic acetate on the water-bath gave a product having the same smell as that from the reaction of sodic acetate on turmerylchloride, but no means could be found of separating it from the unaltered turmerol, as it was decomposed by distillation even *in vacuo*. We accordingly turned our attention to the ethers of turmerol, and selected for study the isobutylether, as the difference between the percentage composition of this and that

of the alcohol would be greater than in the case of the methyl- or ethylethers.

*Isobutylether of Turmerol.*

This body was prepared by boiling the sodium compound with isobutyl iodide in a flask with a return-condenser for some time; the product was purified by distillation *in vacuo*.

I. 0.2110 gram of substance gave 0.6524 gram of  $\text{CO}_2$  and 0.2039 gram of  $\text{H}_2\text{O}$ .

II. 0.2742 gram of substance gave 0.8520 gram of  $\text{CO}_2$  and 0.2646 gram of  $\text{H}_2\text{O}$ .

| Calculated for $\text{C}_{19}\text{H}_{27}\text{OC}_4\text{H}_9$ . |       | Found. |       |
|--------------------------------------------------------------------|-------|--------|-------|
|                                                                    |       | I.     | II.   |
| Carbon                                                             | 84.14 | 84.45  | 84.71 |
| Hydrogen                                                           | 10.97 | 10.73  | 10.83 |

It is a heavy yellowish oil with a pleasant smell. The ethylether is a similar substance.

From the observations described there can be no doubt that turmerol is an alcohol.

*Oxidation of Turmerol.*

When turmerol was treated with a hot aqueous solution of potassic permanganate until it was no longer decolorized, and after destroying the slight excess of permanganate with sodic sulphite the liquid was filtered from the brown hydrate of manganese, upon adding sulphuric acid a yellowish-white precipitate was thrown down, which, purified by washing with alcohol, became perfectly white, and volatilized without melting, indicating that it was terephthalic acid. To prove that this was the case, the acid was converted into the methylester by passing hydrochloric acid through methyl-alcohol, in which it was suspended. The solid gradually dissolved, and upon allowing the alcohol to evaporate, long prisms were deposited, which, after two crystallizations from hot alcohol, melted at  $139^\circ$ – $140^\circ$ . Melting point of methylester of terephthalic acid  $140^\circ$ . Another sample of the acid was analyzed:

0.1782 gram of substance gave 0.3798 gram of  $\text{CO}_2$  and 0.0641 of  $\text{H}_2\text{O}$ .

| Calculated for $\text{C}_8\text{H}_6\text{O}_4$ . |       | Found. |
|---------------------------------------------------|-------|--------|
| Carbon                                            | 57.83 | 58.12  |
| Hydrogen                                          | 3.62  | 4.00   |



The product in this case, therefore, is terephthalic acid, and turmerol must stand in close relationship to the para series of aromatic compounds. It is probably a derivative of the terpenes.

The formation of terephthalic acid from turmeric oil also explains the results of Ivanow-Gajewsky in regard to the oxidation of curcumin, as it renders it almost certain that the terephthalic acid obtained by him, but of which we could find no trace, proceeded from an impurity of turmeric oil in his curcumin.

When cold potassic permanganate not in excess is used, turmerol yields one or more apparently new acids, with the investigation of which we are at present occupied.

#### SUMMARY.

The formula of turmerol (the fraction of turmeric oil boiling from  $193^{\circ}$  to  $198^{\circ}$  under 60 mm. of pressure) is  $C_{19}H_{28}O$ , or, one of its adjacent homologues.

Its alcoholic nature is proved by the following observations:

1. Conversion into  $C_{19}H_{27}Cl$  by hydrochloric acid or phosphorous trichloride. The chlorine can be removed by ordinary reagents.

2. The formation of a compound,  $C_{19}H_{27}ONa$ , by the action of sodium.

3. The formation of its isobutylether,  $C_{19}H_{27}OC_4H_9$ .

That it is related to the para compounds of the aromatic series is proved by its conversion into terephthalic acid by treatment with a hot aqueous solution of potassic permanganate in excess.

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#### ON ETHOXY-METATOLUIC ACID.

By P. H. BROUN.

In a paper<sup>1</sup> recently published, Remsen and Kuhara proved that the nitro-toluic acid obtained by oxidation of ordinary nitro-xylene with chromic acid contains the nitro-group in the ortho-position relatively to the methyl, and in the para-position relatively to the carboxyl. This was shown by converting the nitro-acid into the

<sup>1</sup> This Journal, 3, 426.

corresponding hydroxy-acid, which was found to be ortho-homo-

paroxybenzoic acid  $C_6H_3 \begin{cases} OH & (1) \\ CH_3 & (2) \\ COOH & (4) \end{cases}$ . While the diazo-com-

pound was readily converted into the hydroxy-acid by boiling with water, it was found that, when boiled with alcohol, it did not yield metatoluic acid, the formation of which would naturally be expected, but another acid with markedly different properties. In regard to it the authors say: "This acid is insoluble in cold water, and only slightly in hot water. It crystallizes from an alcoholic solution. It is volatile with steam. It sublimes in light flakes. The analyses did not give satisfactory results. With the small quantity at our disposal it was impossible to determine what the acid is."

At the suggestion of Professor Remsen I have since prepared the acid in larger quantity, and have succeeded in showing what it is.

In the preparation of amido-toluic acid from the nitro-acid I found it advisable to use as little hydrochloric acid as possible, the yield being greatest under these circumstances. The preparation of the diazo-compound requires the greatest precautions. For dissolving the amido-acid very dilute nitric acid should be used. The dilute acid of the strength commonly used for a reagent is much too concentrated. It should be diluted with eight to ten times its volume of water. If this precaution is not taken, the amido-acid may easily be completely decomposed, as happened in two cases in my own experiments.

The dried diazo-compound was boiled with a considerable quantity of absolute (99 per cent.) alcohol. An abundant evolution of gas accompanied the boiling at first. After this stopped, the solution was diluted with water, when the acid under investigation was thrown down, having all the properties ascribed to it by Remsen and Kuhara. It was converted into the calcium salt, which is easily soluble in water, and crystallizes in long, white, silky needles. The analyses of the air-dried salt gave results as below:

I. 0.1364 gram salt lost 0.0119 gram  $H_2O$  at  $170^\circ$ ; and gave 0.0424 gram  $CaSO_4$ .

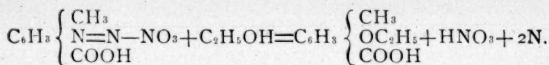
II. 0.1493 gram salt lost 0.0127 gram  $H_2O$  at  $175^\circ$ ; and gave 0.0465 gram  $CaSO_4$ .

These results lead to the formula of the calcium salt of *ethoxy-*

*metatoluic acid*,  $\left( C_6H_3 \begin{cases} CH_3 \\ OC_2 \\ COO \end{cases} \right)_2 Ca + 2H_2O$ .

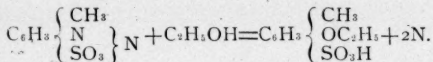
|                  | Calculated. | Found. |       |
|------------------|-------------|--------|-------|
|                  |             | I.     | II.   |
| Ca               | 10.05       | 10.01  | 10.02 |
| H <sub>2</sub> O | 8.29        | 8.72   | 8.51  |

The equation representing the action described is:



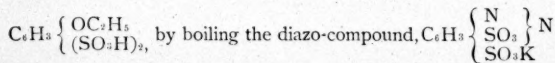
A few transformations of the same kind have already been effected. Thus Hayduck<sup>1</sup> obtained ethoxy-paratoluene-sulphonic

acid,  $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CH}_3 \\ \text{OC}_2\text{H}_5 \\ \text{SO}_3\text{H} \end{array} \right.$ , by boiling with alcohol the diazo-compound from ortho-amido-paratoluene-sulphonic acid:

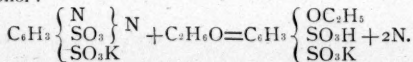


Hayduck found, further, that, when methyl alcohol was used instead of ethyl alcohol, a similar reaction took place, resulting in the formation of a methoxy compound,  $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CH}_3 \\ \text{OCH}_3 \\ \text{SO}_3\text{H} \end{array} \right.$

Later Zander<sup>2</sup> obtained ethoxy-benzene-disulphonic acid,



with alcohol:



He was, however, unable to determine the relation of the groups in the compounds involved in the reaction, and hence it is at present impossible to say whether the same conditions exist in the three diazo-compounds which have yielded the peculiar results. In Hayduck's compound, as well as in that of Remsen and Kuhara, the diazo-group occupies the ortho-position relatively to methyl, and the thought first suggests itself that probably this position of the group is the immediate cause of the peculiar conduct. The

<sup>1</sup>Annalen der Chemie, 172, 215.

<sup>2</sup>Annalen der Chemie, 198, 25.

question arises whether all diazo-groups which occupy the ortho-position conduct themselves in the same way.

I have made some experiments with the object of answering this question, if possible. An attempt was made to study the simplest case, viz. that of orthotoluidine, but the desired transformations were not effected. Experiments with ortho-nitro-parasulphobenzoic acid also gave unsatisfactory results.

I intend, as opportunity may offer, to have further experiments made, similar to that above described by Mr. Broun. It appears probable that this anomalous conduct of diazo-compounds will be found to be connected with the position of the diazo-group.

I. R.

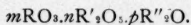
JOHNS HOPKINS UNIVERSITY, December, 1882.

## ON COMPLEX INORGANIC ACIDS.<sup>1</sup>

BY WOLCOTT GIBBS, M. D.

*Rumford Professor in Harvard University.*

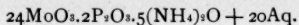
My further investigations of the complex inorganic acids have yielded results of a very interesting character, and the field of work has become so extensive that it is simply impossible for one man to attempt to cover the whole ground. In the papers which I have already published I have described only binary compounds, such as may be expressed by the general formula—



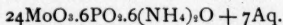
In this formula  $m$  may represent any even number from 10 to 48 inclusive,  $R$  either molybdenum or tungsten,  $n$  is 2 in the compounds described,  $r$ ,  $p$  the number of molecules of base (old style), while  $R'$  represents either phosphorus or arsenic. I have now generalized these results still further. In place of phosphorus or arsenic we may have vanadium or antimony, and probably niobium and tantalum, as I stated long since in a preliminary notice. In place

<sup>1</sup> From a letter to the editor, dated Cambridge, Dec. 11, 1882.

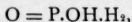
of oxides of the type  $R'_2O_3$ , we may have those of the type  $R'_2O_3$ , as, for example,  $As_2O_3$ ,  $Sb_2O_3$ ,  $P_2O_3$ , and probably  $V_2O_3$ . Thus, the formula of a phosphoroso-molybdate of ammonium is



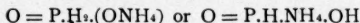
These compounds by oxidation pass into salts containing the higher oxides of the type  $R'_2O_5$ . Salts containing boric oxide,  $B_2O_3$ , have been described by Klein. Even hypo-phosphorous acid is capable of forming similar compounds. Thus, I have obtained a hypo-phospho-molybdate with the formula—



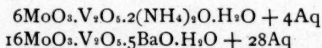
Perhaps further study will show that the analyses may be represented by a simpler formula. A different mode of expression must be adopted, if, with Wurtz, we write the formula of hypo-phosphorous acid:



so that we have, probably, either

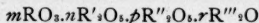


as the term representing the phosphorus contained, the type being still  $O = P \equiv (OH)_3$  as in phosphoric acid, part of the ammonium being united to  $WO_3$  in the structural formula. Well defined and beautifully crystalline vanadio-molybdates have respectively the formulas—



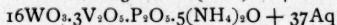
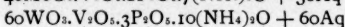
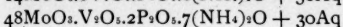
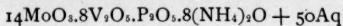
which correspond to types of phospho-molybdates and phospho-tungstates. In like manner in two vanadio-tungstates of sodium the ratios of the tungstic and vanadic oxides are respectively as 10:1 and as 18:1.

Ternary series containing tungstic or molybdic oxide united to two other oxides also exist in large number. Thus, in the general formula—

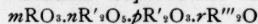
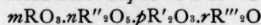
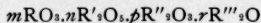


$RO_3$  may be either tungstic or molybdic oxide,  $R'_2O_3$  and  $R''_2O_3$  two different oxides of the same type, as, for example, phosphoric and vanadic oxides. I am not prepared to say that *any* two known oxides of the type  $R_2O_3$  may enter together into such compounds,

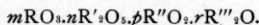
but it is not impossible that such is the case. Examples of these salts are the following :



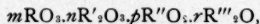
I refrain from theory at present, and simply remark, first, that some of these compounds are almost certainly double salts, and, secondly, that in certain cases very simple formulas are obtained if we suppose that  $\text{V}_2\text{O}_5$ , with the atomic structure  $\text{V}_2\text{O}_5\text{O}_3$ , may replace  $\text{WO}_3$  or  $\text{MoO}_3$ , while with the formula  $\text{V}_2\text{O}_5$  it replaces  $\text{P}_2\text{O}_5$ . Other ternary series contain oxides of two types united to tungstic or molybdic oxide. Thus, we have the general formulas :



in which  $\text{R}_2\text{O}_3$  may be  $\text{P}_2\text{O}_5$ ,  $\text{V}_2\text{O}_5$ ,  $\text{As}_2\text{O}_5$ , or  $\text{Sb}_2\text{O}_5$ , perhaps also  $\text{Nb}_2\text{O}_5$  and  $\text{Tn}_2\text{O}_5$ , and  $\text{R}_2\text{O}_3$  may be  $\text{B}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ ,  $\text{V}_2\text{O}_5$ ,  $\text{As}_2\text{O}_5$ ,  $\text{Sb}_2\text{O}_5$ . You will see that such compounds may be very numerous, especially if  $m$ ,  $n$  and  $p$  may vary within wide limits. There is, however, at least one other group of ternary compounds reducible to the general formula—

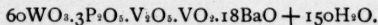


I have obtained a few salts belonging to such series. Finally, it seems probable that there is also a series embraced in the formula—

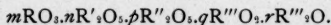


but I have not yet obtained compounds of this type.

Quaternary compounds of various types appear to exist. An example of these is the following :

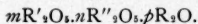


This is almost certainly a double or triple salt, but still shows how five different oxides may exist in a single well-defined and beautifully crystallized compound. The general formula here would be



The possible number of combinations, if we take all the oxides not basic belonging to the four different types, and in addition give various values to  $m$ ,  $n$ ,  $p$  and  $q$ , must be very great.

Besides the types which I have given above I have obtained others of an entirely different character and not containing either molybdenum or tungsten. To this class belong phospho-vanadates, arsenio-vanadates and antimonio-vanadates, the general formula being



The salts are often beautifully crystallized and well defined.

I reserve to myself the right to work in any part of this field of research, since the generalizations are exclusively my own; but at the same time I invite other chemists to enter the same field, probably the widest which has been opened up in the domain of inorganic chemistry. The results which I have given above were communicated to the National Academy of Sciences at the April and November sessions of the present year, but as some little time must elapse before I can fully complete another instalment of my work, I shall be glad if you consider this brief abstract worthy of publication in your journal.

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Contributions from the Chemical Laboratory of Harvard College.

## XXIX.—ON THE ACTION OF PHOSPHORUS TRICHLORIDE ON ANILINE.<sup>1</sup>

### PRELIMINARY NOTICE.

BY C. LORING JACKSON AND A. E. MENKE.

The only paper on this subject which we have been able to find was published by M. Tait<sup>2</sup> in 1865. From the abstract in the *Jahresbericht* it appears that he obtained a semi-solid mass easily soluble in water, alcohol, and ether, which, freed from an excess of aniline, had the composition  $(C_6H_5NH)_3P_3HCl$ , gave a chlorpla-

<sup>1</sup> Presented to the American Academy, Dec. 13th, 1882.

<sup>2</sup> *Jahresbericht* '65, 411. *Instit.* '65, 254.



minate, and several double salts, but yielded no satisfactory result when he attempted to set free the base. As a further investigation of Tait's substance seemed to promise interesting results, and we hoped also to obtain new compounds by varying the conditions of the reaction, we took up the study of this subject, and publish this preliminary notice in the hope of reserving it to ourselves for future work.

On adding phosphorus trichloride drop by drop to aniline as long as it produced a violent action, we obtained a white solid, which to our surprise was entirely different from Tait's product in that it was insoluble in ether, of a much more solid consistency, and on analysis proved to be a variable mixture of some phosphorus compound and aniline chloride, one sample containing 5.7 per cent. of phosphorus, another only 2.9, while the carbon, hydrogen, and chlorine showed as marked variations. We have not made out as yet the cause of this difference between our result and that of Tait, which is the more striking, because we took pains to follow his directions most carefully, but hope that a more complete study of the conditions of the reaction, especially in the presence of solvents, may explain the discrepancy. As the purification of this phosphorus compound offered serious difficulties, owing to its resemblance to aniline chloride in solubility, we have postponed its further study, and for the present confined our attention to one of the products of the action of heat upon it.

When the crude product of the action of phosphorus trichloride and aniline is heated over a free flame in a porcelain dish, it turns orange yellow, and gives off white fumes, which are luminous in the dark and deposit a sublimate of pure aniline chloride, as was proved by analysis. This reaction takes place slowly even at  $100^{\circ}$ , but a rapid heating at a higher temperature, as described, was found to give the best result; on the other hand the heat must not be too great, as in this case phosphoretted hydrogen is given off. The orange product boiled with alcohol gives a colorless solution and an orange residue apparently consisting of solid phosphide of hydrogen, although we have not as yet succeeded in obtaining it perfectly pure. The alcoholic solution upon addition of water throws down a white precipitate, which was purified by repeating twice the solution in alcohol and precipitation with water, and drying at  $60^{\circ}$ . The following analyses show that its formula is  $(C_6H_5NH)_3POH$ . It may be called therefore *dianilido-phosphorus*

hydrate, and is probably formed by the action of the alcohol on a substance  $(C_4H_8NH)_3PCl$ .

I. 0.3488 gram of substance gave 0.7992 gram of  $CO_2$  and 0.1918 gram of  $H_2O$ .

II. 0.2856 gram of substance gave 0.6502 gram of  $CO_2$  and 0.1610 gram of  $H_2O$ .

III. 0.4623 gram of substance gave 49.9 cc. of nitrogen at a temperature of  $25^\circ$ , and a pressure of 766 mm.

IV. 0.3402 gram of substance gave after treatment with  $Na_2CO_3$  and  $KClO_3$  0.1590 gram of  $Mg_3P_2O_7$ .

Calculated for  $(C_4H_8NH)_3POH$ .

|            | Found. |       |       |       |
|------------|--------|-------|-------|-------|
|            | I.     | II.   | III.  | IV.   |
| Carbon     | 62.07  | 62.48 | 62.04 |       |
| Hydrogen   | 5.60   | 6.10  | 6.26  |       |
| Nitrogen   | 12.07  |       | 12.13 |       |
| Phosphorus | 13.36  |       |       | 13.05 |

The substance contains no chlorine. Analyses II, III and IV were of the same preparation. I of a different preparation.

It forms an amorphous white mass with a slight odor of phosphoretted hydrogen; melts, or rather draws together into a viscous state at  $87^\circ$ ; is freely soluble in cold alcohol, still more so in hot, insoluble in water. It is not acted on apparently by either aqueous potassic hydrate or dilute sulphuric acid, but is decomposed by strong nitric acid.

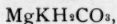
The aqueous filtrate obtained in the purification of the foregoing substance yields on evaporation crystals, which also contain phosphorus. The investigation of the bodies mentioned in this paper, and of the many other substances, which we have reason to expect can be obtained from this reaction, will be pushed forward by us as rapidly as possible.

## REVIEWS AND REPORTS.

ON SOME RECENT IMPROVEMENTS IN INDUSTRIAL CHEMICAL PROCESSES.<sup>1</sup>

(Concluded from page 311.)

The process to which I will next ask your attention is that for the manufacture of carbonate of potash, which has been invented by Professor Engel, of the Faculty of Medicine of Montpellier. Professor Engel has found that if one takes a solution of potassium chloride holding in suspension either magnesia or magnesium carbonate, and treats it by carbon dioxide, with constant agitation, one obtains a solution of magnesium chloride holding in suspension a curious double carbonate of magnesium and potassium. The composition of this double carbonate varies with the temperature employed, and with other circumstances; but, as produced by the mode of operating which Professor Engel proposes to employ industrially, the double carbonate appears to be—



or a compound of one equivalent of bicarbonate of potash with one equivalent of magnesium monocarbonate:



The existence of the double carbonate of magnesium and potassium was first made known, now many years since, by the late Henri Sainte-Claire Deville, who obtained it by the reaction on magnesium chloride of previously-formed bicarbonate of potash used in excess. Deville's method was thus the inverse of Professor Engel's, Professor Engel's double carbonate being produced by the reaction on potassium chloride of bicarbonate of magnesia in presence of magnesium monocarbonate.

As obtained by Professor Engel, the double carbonate is a crystalline powder, capable of being separated from its mother-liquor, readily and completely, by any of the ordinary methods of filtration. While quite insoluble in solution of magnesium chloride, and not at all attacked thereby in the cold, it is decomposed by pure water—slowly and only partially at ordinary temperatures, but at higher temperatures quickly and completely. Professor Engel's method of manufacturing carbonate of potash, therefore, consists in the following successive operations:

1. Injection of  $\text{CO}_2$ , preferably under a pressure of from two to three atmospheres, into a solution of potassium chloride, to which has been added the magnesium carbonate obtained in a previous fourth operation and a suitable quantity of fresh magnesia.

<sup>1</sup> Read before the "Society of Chemical Industry" by Mr. Walter Weldon.

2. Separation, by means of the hydro-extractor, of the resulting double carbonate of magnesium and potassium from the solution of magnesium chloride produced at the same time.

3. Decomposition of the double carbonate, and also of the bicarbonate of potash, which is one of its constituents, by boiling the double carbonate with water. (This operation is performed in closed vessels, in order that the  $\text{CO}_2$  evolved during the reduction of the bicarbonate of potash to the state of normal carbonate may be collected for use again.)

4. Separation, by means of the hydro-extractor, of the solution of potassium carbonate obtained in the third operation from the magnesium carbonate, which it at first holds in suspension.

5. Evaporation of the filtrate from the fourth operation to dryness.

The magnesium carbonate separated in the fourth operation goes back into the next first operation. To it has to be added each time a quantity of fresh magnesia equivalent to the magnesium chloride produced in the first operation. The fresh magnesia is obtained by heating magnesite in a current of steam. Carbon dioxide is of course obtained at the same time, and the  $\text{CO}_2$  from this source, together with that driven off from the double carbonate in the fourth operation, make up, if all loss be avoided, the total quantity of  $\text{CO}_2$  required.

Many years ago, when I was as yet without any practical chemical experience, and was foolish enough to think that a merely literary acquaintance with chemistry was sufficient to enable one to invent new industrial chemical processes, I secured a patent for treating sodium chloride exactly as Professor Engel treats potassium chloride. I expected that by so doing I should obtain magnesium chloride and bicarbonate of soda. Subsequent experience showed that while sodium chloride can be decomposed by bicarbonate of magnesia, if sufficient pressure be used, the amount of pressure required is far too great to permit of the reaction being performed industrially; and to this fact is due a merit of Professor Engel's process which is of very great practical moment. We know that, for many of the purposes for which carbonate of potash and caustic potash are used in the arts, the presence with them of even only minute quantities of soda is very prejudicial; and we also know that nearly all commercial potassium chloride has associated with it appreciable proportions of sodium chloride. From a mixed solution of potassium and sodium chlorides, however, Professor Engel's process will precipitate the whole of the potassium as double carbonate, the whole of the sodium chloride remaining in solution, absolutely unchanged. On the sole condition that the double carbonate produced by his first operation be washed completely free from mother-liquor, as it readily may be, his final product must, indeed, be almost chemically pure. It cannot contain any foreign bodies whatever, except such as it may

take up from the material of the vessels in which the filtrate from the fourth operation is evaporated down.

Though the Engel process is not yet in industrial operation, active steps are being taken to the end that it soon shall be. The process was tested on a semi-industrial scale at Montpellier last spring, and the results obtained led to the formation of a "Société de Carbonate de Potasse"—to which I have been invited to become Ingénieur Conseil—and this Société began some months ago to build a factory at Havre, and has just bought land for a second factory at Stassfurt. The factory at Havre is expected to be at work before the end of this year.

Another French process for the manufacture of carbonate of potash is further advanced. I refer to the trimethylamine process, which the Société de St. Croix, whose works are situated near Lille, is now practising on a somewhat considerable scale. We all know that the "ammonia process," now so largely used for the manufacture of soda, cannot be used for the manufacture of potash, by reason of hydro-potassic carbonate being too soluble in solution of ammonium chloride. Bicarbonate of potash, however, is but very slightly soluble in solution of chloride of trimethylamine; and trimethylamine, thanks to the admirable invention of my friend, Professor Camille Vincent, of the École Centrale, is now placed, as the French say, at the door of all the world. Though so rare a substance a very short time ago, it is now cheaper, I believe, equivalent for equivalent, than ordinary ammonia. I am not acquainted with the details of the process by which the Société de St. Croix manufactures potash by means of this compound ammonia. I am not acquainted with any of the members of that Société, and I am told that they wish to keep the details of their process secret. An account of the theory of the process, however, was recently published by its inventors, MM. Ortlieb and Müller, in the *Bulletin Scientifique du Département du Nord*; and as that journal probably does not circulate largely among the members of this Society, and as I have not seen the memoir of MM. Ortlieb and Müller copied into any other journal, I may perhaps be allowed to briefly indicate the chief point which it brings out. The chemistry of the trimethylamine potash process appears to differ from that of the ammonia soda process otherwise than merely in the nature of the ammonia employed. The first step in the ammonia-soda process is to form ammonia bicarbonate; but no bicarbonate of trimethylamine is known to exist. The highest carbonate of trimethylamine which can be obtained in the free state, under any conditions at present known, is the sesquicarbonate; and the reaction of sesquicarbonate of trimethylamine upon potassium chloride, if indeed, strictly speaking, any such reaction can be said to take place at all, is more complex than the reaction upon sodium chloride of bicarbonate of ordinary ammonia. In the latter case we have an ordinary double decomposition, followed or accompanied by a not very large amount of inverse reaction. We may

say that all the ammonium bicarbonate undergoes conversion into ammonium chloride, and that all the sodium chloride undergoes conversion into bicarbonate of soda, but that the whole of the bicarbonate of soda formed does not precipitate, owing to this salt being as soluble in solution of ammonium chloride as in pure water, and that between a part of that portion of it which dissolves in the mother-liquor and some of the ammonium chloride of the mother-liquor, reverse reaction takes place. Still, the essential reaction of the ammonia-soda process is of the nature of a simple interchange of constituents between two salts, reacting upon each other, equivalent for equivalent. With sesquicarbonate of trimethylamine and potassium chloride, however, the case is otherwise. One has to use several equivalents of sesquicarbonate of trimethylamine per equivalent of potassium chloride, and one obtains, mixed with sesquicarbonate of trimethylamine, which has undergone no change, one equivalent of bicarbonate of potash, one equivalent of chloride of trimethylamine, and one equivalent of what MM. Ortlieb and Müller call sub-sesquicarbonate of trimethylamine, being a body containing four of trimethylamine and five of carbonic acid. MM. Ortlieb and Müller explain what takes place by supposing that sesquicarbonate of trimethylamine is really a compound of sub-sesquicarbonate with an unstable bicarbonate, incapable of existing by itself; and that in their process a portion of the sesquicarbonate splits up into these two constituents, of which the latter only then reacts upon the potassium chloride. Be that as it may, it would seem that to decompose one equivalent of potassium chloride MM. Ortlieb and Müller require to use six equivalents of trimethylamine and nine equivalents of carbonic acid. And yet it is certain that their process is so far a commercial success that the German manufacturers of potash by the Leblanc process are already feeling the competition of the Société de St. Croix very keenly.

I may just add that the trimethylamine process is available for the manufacture of potash only from potassium chloride. Upon potassium sulphate, sesquicarbonate of trimethylamine has no action. Hence the Société de St. Croix cannot use the potash salts—15 or 16 per cent. of which are sulphate—of which some four or five thousand tons a year are produced in their own Department of France from the residue of the distillation of alcohol from the product of the fermentation of the molasses produced in beet-root sugar factories; but they have to fetch their potassium chloride all the way from Stassfurt. The fact that they can, nevertheless, compete with the German makers by the old process is of course all the more remarkable.

The Engel process is not thus limited as regards its raw material. It can transform potassium sulphate into carbonate as readily as potassium chloride.

Some expectation has been entertained that trimethylamine might be used instead of ordinary ammonia in the ammonia-soda process;

and MM. Ortlieb and Müller show that sesquicarbonate of trimethylamine reacts upon both sodium sulphate and sodium chloride in the same manner as upon potassium chloride. To substitute, however, six equivalents of a body having a high molecular weight for one and a half to two equivalents of a body having a much lower molecular weight, would be hardly rational; and we may therefore take it that the industrial applications of trimethylamine will be confined to purposes to which ordinary ammonia is not applicable.

I can hardly pass from the trimethylamine potash process without expressing my curiosity as to how the Société de St. Croix has got over the difficulty which one would have thought there must have been to get workmen to manipulate trimethylamine. I have not worked with trimethylamine myself, and I am acquainted with its peculiar odor only by reputation. From all I am told, however, that acquaintance with it is quite close enough. Friends in France have more than once offered me a few litres of trimethylamine for my laboratory, but always with a strong recommendation that I should not accept them. They assure me that the odor of very putrid herring is almost pleasant in comparison with that of commercial trimethylamine, and that the latter is not only so powerful and offensive but also so clinging and persistent that to merely pour a little trimethylamine from a bottle into a beaker is to condemn yourself to seclusion from all decent society for a somewhat considerable time. How the Société de St. Croix manages in this matter I should like to know.

I have only one other new French process to touch upon, and that is the process of MM. Benker and Lasne for economizing nitrous compounds in the manufacture of sulphuric acid. Some of the members present are perhaps only too well aware that the whole of the nitrous compounds contained in the gases from the vitriol-chambers does not undergo absorption in the Gay-Lussac tower, and MM. Benker and Lasne believe that they have proved that one reason of this is that  $\text{NO}_2$ , at any rate under the conditions which obtain in the Gay-Lussac tower, does not form with sulphuric acid any stable compound. A portion, at any rate, of the nitrous compounds in the exit-gases from the vitriol-chambers is unquestionably there as  $\text{NO}_2$ , and some authorities are of opinion that  $\text{NO}_2$  can, and does in the Gay-Lussac tower, react on sulphuric acid, forming nitrosulphonic acid and nitric acid, both of which are then retained in solution by the excess of sulphuric acid, which is of course always present. MM. Benker and Lasne hold, on the contrary, that the only oxide of nitrogen which can form a stable compound with sulphuric acid is nitrous anhydride, or  $\text{N}_2\text{O}_3$ ; and, therefore, that for the  $\text{NO}_2$  in the chamber-gases to be absorbed in the Gay-Lussac tower, it must be reduced to  $\text{N}_2\text{O}_3$  before it reaches the Gay-Lussac tower. In order thus to reduce the  $\text{NO}_2$  in the chamber-gases before these reach the Gay-Lussac tower, MM. Benker and Lasne inject into the conduit conveying the exit-gases from the last chamber to the foot of the Gay-Lussac

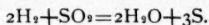


tower a regulated quantity of  $\text{SO}_2$ , accompanied by just the quantity of vapor of water necessary to form, with the  $\text{SO}_2 + \text{NO}_2$ , nitrosulphonic acid. There can be no doubt that in one or two French works this expedient has reduced the consumption of nitre, per given quantity of sulphuric acid produced, to less than one-half the lowest proportion to which it had ever previously been reduced in any sulphuric acid work whatever; but in some other French works, and in several English works into which I have been the means of introducing MM. Benker and Lasne's process, it has not as yet given equally satisfactory results. This can only be due to some difference between the mode in which the chambers are conducted in the works in which the process gives good results, and the mode in which the chambers are conducted in the works in which it has as yet been less successful; but what the nature of that difference is has for some months past puzzled us greatly. MM. Benker and Lasne, however, now believe that they have at last solved the difficulty; and I am going to Paris to-morrow to learn how.

A plan of another kind for accomplishing the same object has just been patented by the *Compagnie de St. Gobain*. I have no details of its results, though I hope to visit Chauny and obtain such this week. It consists in making the gases which have traversed the ordinary Gay-Lussac tower afterwards traverse several supplementary towers, supplied with weaker sulphuric acid than is supplied to the Gay-Lussac tower itself. I am informed that the acid running from the supplementary towers is found to contain dissolved in it appreciable quantities of nitric acid.

From the "pleasant land of France" I will now ask you to pass for a few moments to a spot on the banks of the Elbe, situated at the northern extremity of the district known as "Saxon Switzerland," the interest of which district, due to its wonderful picturesqueness, and to the association of so many points of it with song and legend, is heightened to some minds, including my own, by the fact that the rocks by which its mountains are chiefly composed contain not less than 11 per cent. of potash and 4 per cent. of lithia. I refer, of course, to Aussig, in Bohemia. At the splendid works of Dr. Max Schaffner, at Aussig, my friend and fellow-member, Mr. J. C. Gamble, and myself saw in operation, on an experimental scale, three years ago, a process for recovering sulphur from alkali-waste, which, with some modifications, is now likely to prove of very exceptional importance. This method, the joint invention of Dr. Schaffner and Mr. W. Helbig, the manager of the Aussig works, differs from all other processes for the same object which have attained any measure of practical success in three very important particulars. All other processes consume hydrochloric acid, recover only a portion of the sulphur contained in the waste treated, and recover none of the calcium contained in it; but Messrs. Schaffner and Helbig's process requires no acid, recovers the whole of the sulphur originally contained in the waste, and, in

addition, recovers all its calcium as carbonate. As originally devised and as Mr. Gamble and I saw it in operation on the occasion in question, it included three operations, the first of which consisted in heating fresh waste with solution of magnesium chloride, in a closed iron vessel furnished with a mechanical agitator. Under such circumstances two successive, though practically simultaneous double decompositions take place. Calcium sulphide and magnesium chloride decompose each other, producing calcium chloride and magnesium sulphide, and then this last reacts upon some of the water present to produce magnesia and sulphuretted hydrogen. The sulphuretted hydrogen is evolved in a continuous stream until the charge of waste is completely decomposed, and there then remains in the boiler a solution of calcium chloride holding in suspension an equivalent of magnesia. MM. Schaffner and Helbig pointed out to us that as the sulphuretted hydrogen obtained in this way cannot but be absolutely pure, its application to the production of  $\text{SO}_2$  for use in vitriol-chambers would be free from all the inconveniences experienced when attempting to manufacture sulphuric acid from such mixtures of sulphuretted hydrogen and carbon dioxide as are obtained by treating the ammoniacal liquors of gas-works by an acid; but they then preferred to treat their sulphuretted hydrogen for the obtainment of free sulphur from it. They had discovered a very simple means of realizing the theoretical reaction:



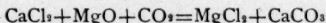
All others who had tried treating together  $\text{H}_2\text{S}$  and  $\text{SO}_2$  had found that the product consisted largely of pentathionic acid; but MM. Schaffner and Helbig had found that if the two gases be caused to react upon each other in presence of not less than a certain quantity of solution of either calcium chloride or magnesium chloride, either no pentathionic acid is formed at all, or, if any be formed, it is immediately decomposed, with a result that all the sulphur of both gases is obtained in the free state. The second operation which Mr. Gamble and I saw at Aussig was accordingly conducted as follows: First, one-third of the sulphuretted hydrogen was burnt into  $\text{SO}_2$  and steam. (Some two hundredweight or so of sulphur were being produced per day, but the operation of burning one-third of the  $\text{H}_2\text{S}$  corresponding to that quantity of sulphur consisted simply in permitting the  $\text{H}_2\text{S}$  to issue from a couple of fish-tail burners, and then setting light to it, when the jets of  $\text{H}_2\text{S}$  went on burning as regularly and placidly as jets of coal-gas could have done.) Secondly, the products of the combustion of one-third of the  $\text{H}_2\text{S}$  were mixed with the other two-thirds of it, and the resulting mixture was then sent in at the bottom of a small tower, packed pigeon-hole fashion, with blocks of wood, down which was kept trickling solution of calcium chloride. There continually issued from the bottom of the tower a thin

magma, consisting of solution of calcium chloride holding in suspension free sulphur. After the separation of the sulphur by filtration the solution of calcium chloride was used again indefinitely.

By these two operations, then, practically the whole of the sulphur of the waste treated was obtained in the free state. The remaining operation consisted in injecting  $\text{CO}_2$  into the solution of calcium chloride holding magnesia in suspension which had been obtained as the residual product of the first operation, thereby reproducing the quantity of magnesium chloride which had been commenced with, and at the same time regenerating all the calcium carbonate which had been employed for the production of the black ash of which the waste had been one of the constituents. The net result of the three operations thus was that from the waste treated were obtained practically all its sulphur in the free state, and practically all its calcium as carbonate, without consumption of anything but coal and labor.

What appeared to me the weak point in this very remarkable process lay in its third operation. I had had some experience of the reaction upon which that third operation is based some eleven or twelve years before, when I had endeavored by the same reaction to transform into magnesium chloride the calcium chloride obtained by decomposing manganese chloride by lime; and I am afraid that to the impression then made upon my mind by the comparative slowness of the reaction in question is at least partially due the fact that nothing was done in this country with MM. Schaffner and Helbig's process until a few months ago, when it was taken in hand by one of our Vice-Presidents, Mr. Alexander Chance, of Birmingham, who has since been experimenting upon it with a degree of spirit and liberality which I cannot enough admire. Before I had seen the process in experimental operation at Aussig, Dr. Schaffner had asked me, and I had agreed, to undertake its exploitation in this country; and after having seen it, I brought it under the notice of nearly all those English manufacturers of alkali who make chlorine as well; but as I could not tell them either that Dr. Schaffner was himself performing the process on an industrial scale, or that I could regard the industrial practicability of its third operation as being as yet absolutely established, none of them cared to do more than discuss the matter. Mr. Chance does not make chlorine—I have rarely occasion to meet alkali manufacturers who are not also chlorine manufacturers—and Mr. Chance first learnt of the process from Dr. Lunge's book. He immediately began to experiment with it on a scale, not of hundred-weights, but of tons of waste per operation, and he soon came to see that if the whole of the  $\text{H}_2\text{S}$  evolved in its first operation were burned, and the resulting  $\text{SO}_2$  sent into the vitriol-chambers, the cost of the process would be practically simply the cost of the operation of regenerating the magnesium chloride. To convey the waste from the vats to the "stills" in which it is to be treated by magnesium chloride is certainly no more costly, and in many cases

would be much less costly, than the methods of disposing of it which are at present in use; and the temperature to which it suffices to raise the contents of the still is so low, and the reaction which goes on in them takes place so readily, that the cost of the operation for steam and superintendence must be more than counterbalanced by the less cost for labor and plant of obtaining  $\text{SO}_2$  by combustion of  $\text{H}_2\text{S}$  than the cost for the same items of obtaining  $\text{SO}_2$  by the combustion of the sulphur in pyrites. The manufacturer can therefore afford a certain amount of pumping for the regeneration of his magnesium chloride, apart from the consideration that the calcium carbonate regenerated at the same time will at least pay a part, if not the whole, of the cost of it. It is to this point of the regeneration of the magnesium chloride that Mr. Chance has recently devoted his chief attention. Mr. Chance is with us this evening, and I believe he is prepared to tell you that he regards the industrial practicability of the reaction

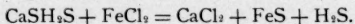


as being now *un fait accompli*.

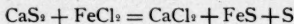
While, however, Mr. Chance has thus been devoting a very rare amount of skill and enterprise and enthusiasm to the industrial realization of the third operation of the original form of MM. Schaffner and Helbig's process, those gentlemen themselves have been endeavoring to so modify their process that that third operation shall, at least in certain cases, be no longer necessary. I am extremely sorry that I have not as yet permission to make the new form of their process public. I hope to have the privilege of bringing it before you on some future occasion; but all that I can say of it now is that it provides for the regeneration of the magnesium chloride by a method which involves no pumping at all, and which is entirely paid for by subsidiary advantages. The new method is not one which will be absolutely universally available. The original method will still have to be resorted to in some cases. But between the two methods I feel the utmost confidence that the good old Leblanc process—for, although somewhat of a Radical in politics, and somewhat of a *révolutionnaire* in relation to the chemical industries, I am almost a Tory in respect of what has certainly been hitherto the most important and beneficent industrial chemical process ever invented—I feel, I say, completely convinced that the Leblanc process, instead of being superseded by the ammonia process, will at least be able to hold its own side by side with the ammonia process; that it will be possible by-and-by to render the Leblanc process as inoffensive as the ammonia process; and that, eventually, manufacturers using the Leblanc process will not only cease to accumulate waste-heaps, but become as independent of pyrites-mines as manufacturers of chlorine are of mines of manganese.

The process of MM. Schaffner and Helbig, however, is available only for the alkali-waste of the future—that is to say, it is available

neither for old waste nor for the yellow liquors given off by old waste-heaps. The present waste-heaps, for years after all addition to them shall have ceased, will continue to give off yellow liquors; and wherever these liquors can be collected it will be necessary to collect them, and to treat them for the recovery of sulphur from them. It has seemed to me that there are one or two localities in which one could treat these liquors very economically by a method, which, unlike those practised by Mr. Mactear at St. Rollox, and M. Pechiney at Salindres, would not require any hydrochloric acid. Instead of hydrochloric acid one might use, it seems to me, the solution of iron chloride, which is a residue of the wet process of extracting copper from burnt pyrites. There are watercourses within my knowledge which are continually receiving both the drainage from waste-heaps and copper-extractors' residual liquor. One of the results is, of course, a horrible pollution of the neighboring atmosphere by sulphuretted hydrogen, this sulphuretted hydrogen being, at least mainly, due to the reaction—



The other reaction which takes place when the drainage from waste-heaps comes into contact with ferrous chloride may be represented by the equation—



so that the total products of the reaction of ferrous chloride on yellow-liquor are calcium chloride, ferrous sulphide, free sulphur, and sulphuretted hydrogen. If, however, there were present with the ferrous chloride a sufficient quantity of any oxide of iron, the sulphuretted hydrogen would be decomposed as it was formed, and the final result would be simply a mixture of ferrous sulphide and free sulphur suspended in solution of calcium chloride. The mixture of ferrous sulphide and free sulphur would at first be bulky, but if it were simply left in heaps for a time—say, on the top of the waste-heaps themselves—it would diminish in bulk, and its ferrous sulphide would, for the most part, become oxidized into  $\text{Fe}_2\text{O}_3$  and free sulphur. The sulphur of the mixture could then be readily burned off, if not in ordinary pyrites-burners, certainly in the so-called “shelf-burners” which are so generally used on the Continent, and are now coming into extensive use in this country. To turn to account in this way, however, the ferrous chloride of copper-extractors' residual liquors, it would be necessary first to free those liquors from the sodium sulphate they contain, as otherwise the mixture of ferrous sulphide and free sulphur would be mixed with more than its own weight of calcium sulphate. For this purpose I would propose to employ a third residual product—namely, the solution of calcium chloride, which is the only residual product of the manufacture of chlorine. The operations to be performed would thus be two. First, copper-extractors' residual liquor and solution of calcium chloride should be pumped

simultaneously into a large wooden vessel furnished with a mechanical agitator, and then, when the right proportion of each liquor has been pumped in, the contents of the vessels should be run on to a filter-bed, from which the filtrate should flow to a second wooden vessel furnished also with a mechanical agitator. In this second vessel there should be added to the filtrate either the quantity of lime necessary to decompose a part of the ferrous chloride, so as to produce a quantity of ferrous protoxide equivalent to the quantity of  $\text{H}_2\text{S}$  which would otherwise be evolved in the second operation, or preferably, a quantity of finely-divided  $\text{Fe}_2\text{O}_3$  residue of the operation of burning of the sulphur from a previously-formed quantity of final product. The second operation would then consist simply in pumping into this second vessel yellow-liquor as long as it continued to be decomposed. I think that this manner of proceeding would be effective; it certainly would not be costly; and for two very offensive solutions which now pollute the streams, and also, by one of the products of their reaction on each other, the atmosphere of certain districts, it would substitute an innocuous solution of calcium and sodium chlorides.

In conclusion, I would beg to touch for a moment on a recent improvement in the manufacture of chlorine. In the process by which nearly the whole of the chlorine made in the world is now manufactured, aqueous hydrochloric acid is treated by a "mud" consisting of a compound of artificial manganese dioxide with lime and other protoxides suspended in solution of calcium chloride. If the hydrochloric acid employed were pure, the only products of this treatment would be free chlorine and a residual mixed solution of manganese and calcium chlorides: but as the hydrochloric acid used always contains sulphuric acid, calcium sulphate is formed also; and before the solution can be treated for the reconversion of its manganese into a state in which it can again liberate chlorine from  $\text{HCl}$ , this calcium sulphate has to be got rid of. To this end, the solution is allowed to repose until the calcium sulphate is deposited; the clear part of the solution is then decanted, and the residual mixture of calcium sulphate and mother-liquor is then passed through the filter-press. These operations all involve a certain amount of cost. While the calcium sulphate is being allowed to settle, the solution cools, and the heat which it thus loses has afterwards to be restored to it; the treatment of the deposit by the filter-press costs at least something for labor and steam; and though the filter-press separates from the magma of calcium sulphate and mother-liquor the greater portion of the latter, it does not separate the whole, and there is therefore lost with the calcium sulphate a certain proportion of manganese chloride. These inconveniences have led to many attempts to purify from sulphuric acid the hydrochloric acid used in the manufacture of chlorine before admitting it into the chlorine stills; but no such attempt had practically succeeded until about a year ago, when Mr. W. G. Strype, C. E., of the Dublin and Wicklow Manure

Company's works, at Wicklow, realized a method of purifying hydrochloric acid from sulphuric acid by means of calcium chloride. While calcium sulphate is somewhat freely soluble in hot hydrochloric acid, it is only slightly soluble in cold hydrochloric acid; and what Mr. Strype therefore does is to add to his hydrochloric acid, in the cold, about 20 per cent. of its volume of the solution of calcium chloride, which is obtained as a by-product of the regeneration of his manganese, and which, therefore, costs him nothing. He finds that he can thus precipitate as calcium sulphate, very nearly, though not quite, the whole of the sulphuric acid originally present in his hydrochloric acid; and a very simple filter, which he has devised for the purpose, enables him to separate his purified hydrochloric acid from the calcium sulphate so formed at a barely appreciable expense.

When Mr. Strype informed me of the results of his preliminary experiments on this matter, I at once saw that they opened the way to the realization of a method of working in the manufacture of chlorine which would effect a very important economy, additional to those already indicated. Even artificial, finely-divided, hydrated manganese dioxide will not react upon aqueous hydrochloric acid of more than a certain degree of dilution. Hence, when one adds gradually to hot aqueous hydrochloric acid that "manganese mud" of which I spoke, there comes a moment when the mud will no longer dissolve integrally. The acid in the "stills" in which the operation is performed has become so dilute that the only constituents of the mud which it can now react upon are the protoxides in it. If, after this point has been reached, one went on adding mud, the protoxides in the further quantity of mud added would completely neutralize the remainder of the acid, but the  $\text{MnO}_2$  of this further quantity of mud would remain undissolved. When working with hydrochloric acid containing sulphuric acid, one cannot thus add mud after it ceases to dissolve completely, because, if one did, one would obtain a residual solution holding in suspension not only  $\text{MnO}_2$ , but also  $\text{CaSO}_4$ ; and one could not remove the  $\text{CaSO}_4$  from this solution without also removing, and losing, the  $\text{MnO}_2$ . The custom has therefore been, and still is, everywhere except in Mr. Strype's works, to cease sending mud into the chlorine stills when the moment has arrived at which, if more mud were added, the  $\text{MnO}_2$  in it would not dissolve; and when that moment has arrived the contents of the stills are run off into "wells," in which they are then agitated, for the neutralization of the free acid remaining in them, with finely-divided limestone. The acid which is so neutralized by limestone is, of course, lost; the limestone employed to neutralize it is also lost; and the operation of neutralization requires an appreciable amount of steam and labor. I suggested to Mr. Strype that his purified acid would enable him to avoid both this loss of acid and this consumption of limestone; and I am glad to be able to say that the suggestion has been realized. During nearly the whole of last



year Mr. Strype has worked, and he is still working, as follows: Using in his stills hydrochloric acid from which he has first separated the greater portion of the sulphuric acid originally contained in it, he conducts his stills in the ordinary way, running off from them acid "still-liquors" into the ordinary neutralizing wells, but there treating the acid liquors—not absolutely every time, but by far the greater number of times—instead of with limestone dust with manganese mud. The neutralization of the acid liquors by manganese mud occupies only a few minutes; and when the neutralized liquors reach the settlers, the  $MnO_2$  in suspension in them settles so rapidly as to permit settled liquor to reach the oxidizers at such a temperature as not afterwards to require the usual "heating-up" by injection of steam. The  $MnO_2$  which deposits in the settlers is from time to time added to the ordinary mud used in the stills. As Mr. Strype's purified hydrochloric acid, however, still contains a little sulphuric acid, and as calcium sulphate accordingly gradually accumulates in his mud, from time to time he has to intercalate an operation of neutralization by the old way; but this happens only so rarely as to still leave it practically the case that the method of working which he has adopted, besides economizing apparatus, steam and labor, and reducing the loss of manganese to considerably below one per cent., also economizes all the limestone used by others for the neutralization of their still-liquors, and at the same time the quantity of acid equivalent to that quantity of limestone. Mr. Strype thus obtains seven tons of bleaching powder from the quantity of acid from which no one else at present gets more than six tons, and from which very few manufacturers get so much as six tons, while, moreover, realizing appreciable economies at all other points.

#### PHYSIOLOGICAL OXIDATION.

One of the first attempts to explain, by experimental methods, the oxidation processes which take place in animal bodies was made by Schmidt<sup>1</sup> in 1862. Finding that the red corpuscles have the power of giving a deep blue color with guaiac tincture, he concluded that ozone was present in the blood. Schönbein<sup>2</sup> was also of the opinion that physiological oxidation is brought about by ozone in the blood, but subsequent investigations by Huizinga,<sup>3</sup> and more recently those of Nasse,<sup>4</sup> have shown that, not only is ozone absent in animal bodies, but that oxidation is due to atomic or active oxygen. Hoppe-Seyler and his pupils have found that oxygen combined with hæmaglobin does not effect oxidations, and that oxyhæmaglobin is very probably a compound consisting of a

<sup>1</sup> On ozone in the blood. Dorpat, 1862.

<sup>2</sup> Sitzungsber. d. bayr. Acad. d. Wiss. zu München 1, 274.

<sup>3</sup> Virchow's Archiv, 42, 359.

<sup>4</sup> Pflüger's Archiv, 3, 205.

molecule of hæmaglobin united to a molecule of oxygen ( $\text{Hb} + \text{O}_2$ ). It has also been shown that very little oxidation takes place in the blood, but that it takes place mainly in the tissues themselves. These facts lead us to conceive of the process of physiological oxidation as being carried on somewhat in the following way: The atmospheric oxygen is taken up by the blood in the lungs, and, uniting with the hæmaglobin, it forms a compound which of itself has no oxidizing power. In the capillaries this oxyhæmaglobin is dissociated, the oxygen  $\text{O}_2$  passes through the walls of the capillaries into the surrounding tissues, and there in some way is made active, *i. e.* is decomposed into its atoms, and these unite with the oxidizable constituents of the tissues.

Various hypotheses have been suggested to account for the active condition of oxygen in the tissues; prominent among these is that of Hoppe-Seyler.<sup>1</sup>

In studying the processes of putrefaction he observed that free hydrogen is given off in those cases in which oxygen is not present, and that whenever oxygen has access to decaying liquids, not only is all the hydrogen oxidized, but energetic oxidation processes are observed as well. The simplest explanation of this seemed to be that the nascent hydrogen has the power of splitting up the oxygen molecule, uniting with one atom and setting the other free; and to the free atoms thus formed are to be attributed the strong oxidations which take place in decaying bodies. To test this hypothesis he made experiments with palladium hydrogen. The energetic reducing powers of this compound were described by Graham; that it can also cause oxidation, Hoppe-Seyler showed by bringing some strips of palladium foil charged with hydrogen into a solution of indigo in the presence of air. The solution soon became yellow, and after a time the indigo was completely destroyed. If palladium hydrogen be brought into a neutral solution of potassium iodide and starch, the liquid becomes blue in a few minutes, after which the starch is slowly destroyed. In a similar way benzene was oxidized to phenol; so, too, petroleum ether when brought in contact with sodium and exposed to the air takes up oxygen and forms small quantities of volatile acids. "These experiments and others of a similar nature," he asserts, "admit of no explanation other than that the active hydrogen renders the oxygen active, and, since the former unites with oxygen, we cannot well conceive of the process without supposing that the hydrogen in uniting with one atom of the molecule  $\text{O}_2$  sets the remaining atom free, thus making it active." "Just as the hydrogen atom cannot exist in a free state, so the active oxygen, if no oxidizable material is present, unites with water to form hydrogen dioxide, or with inactive oxygen to form ozone."

In common with Claud Bernard and E. Mitscherlich, Hoppe-Seyler compares the life of organisms to a process of decay, and

<sup>1</sup> Zeitsch. phys. Chem. 2, 22. Berichte d. deutsch. chem. Gesells. 12, 1551.

states that, although our knowledge of the processes which take place in the organs of plants and animals is so fragmentary that but few trustworthy facts are known upon which to base the comparison, still he regards it as neither premature nor superfluous to carry it out as far as possible, because there are no facts known which disprove it, and because it affords starting points for future investigations. Just as decaying substances give off nascent hydrogen which, in the presence of oxygen, can make the latter active, so in animal tissues he is inclined to assume that the oxygen is rendered active by the same means.

Closely related to this hypothesis are the recent investigations of Moritz Traube on the active condition of oxygen. His first paper, in which he considers the formation of hydrogen dioxide by oxidation processes, was reviewed in an earlier number of this journal, Vol. 4, p. 73. In a second communication<sup>1</sup> on the theory of the formation of active oxygen by means of nascent hydrogen and palladium hydrogen, he considers Hoppe-Seyler's hypothesis in detail. In regard to the occurrence of hydrogen in animal bodies he says: "Hitherto this gas has only been detected in the alimentary canal, where, as is well known, processes of decay are brought about by bacteria. If putrefaction and life are similar from a chemical standpoint, then in animal bodies soon after death when respiration has ceased, hydrogen should be evolved, for decaying animal matter in the absence of oxygen is known to give off hydrogen. This is by no means the case. An accumulation of gas-bubbles in the blood, or a swelling of the tissues of an animal which has been dead but a short time, has never been noticed. On the contrary, blood and muscles may be preserved at ordinary temperatures for days without becoming charged with gases."

"The researches of van den Broeck<sup>2</sup> have shown that fresh blood, albumen, etc., may be preserved for several weeks, when bacteria are excluded, without a trace of gas being formed. There is, therefore, no observation known which even suggests the formation of hydrogen in the animal body."

He now describes some experiments which were undertaken to show that there is a distinct difference between putrefaction brought about by bacteria and the vital processes of animals. A piece of decaying meat treated with a solution of potassium nitrate was allowed to stand five hours. On testing the solution with iodide of zinc and starch a distinct reaction for nitrous acid was obtained. A piece of fresh muscle treated in the same way gave the reaction for nitrous acid only after standing for three days, when decomposition had begun. Nascent hydrogen cannot therefore be present in muscles, for in a short time the nitre would have been reduced, not to nitrous acid, but to ammonia.

A second characteristic property of bacteria is their power of transforming nitrogenous nourishment into ammonia compounds.

<sup>1</sup> *Berichte d. deutsch. chem. Gesell.* **15**, 2421.

<sup>2</sup> *Annalen der Chemie*, **115**, 78.

Decaying liquids always become ammoniacal, but animal bodies contain only traces of ammonia compounds, and in the normal state neither the tissues nor the secretions and excretions give an ammoniacal reaction. Traube therefore concludes that the transformation of matter in animals is evidently different from that in bacteria; and, as it has been shown that hydrogen is not formed in the tissues, we cannot suppose that the formation of active oxygen in animal bodies is due to nascent hydrogen.

He now considers the chemical part of the hypothesis, viz. that nascent hydrogen can render oxygen active. Hoppe-Seyler's experiment with petroleum ether and sodium he shows to be unreliable, and calls attention to the fact that Fudakowski<sup>1</sup> has shown that petroleum benzine has the power of taking up oxygen at ordinary temperatures without the presence of sodium. He then made the following experiments: Nascent hydrogen was prepared by the action of dilute sulphuric acid on zinc; that the hydrogen at the moment of its liberation is exceedingly active, and has reducing powers which are not possessed by the molecules of hydrogen gas at ordinary temperatures, is well known. Now this nascent hydrogen, when brought in contact with oxygen, if Hoppe-Seyler's hypothesis is correct, should give active oxygen or ozone. But not a trace was formed. And thinking that an objection might be raised by supposing the ozone to be destroyed by the zinc, he added indigo sulphuric acid (which can be easily oxidized) to the sulphuric acid. On adding strips of zinc to the solution, and shaking for twenty minutes, the blue color was not destroyed, showing that neither active oxygen nor ozone was formed. Nascent hydrogen made by the action of zinc on caustic soda was shaken with air and ammonia; if active oxygen had been formed, some of the ammonia would have been oxidized to nitrous or nitric acid, but the experiment showed that not a trace of either was formed. Traube, therefore, regards it as proved that nascent hydrogen has not the power of forming active oxygen, and further shows that nascent hydrogen cannot form hydrogen dioxide with oxygen in the presence of water, because the hydrogen reduces the dioxide, forming water.

These experiments led him to suspect that the oxidations observed by Hoppe-Seyler with palladium hydrogen were not brought about by nascent hydrogen. A simple experiment with palladium hydrogen showed that it too, like zinc and other substances which oxidize in the presence of air and water, has the power of forming hydrogen dioxide. In previous experiments he had shown that when zinc is oxidized under these conditions, no ozone or active oxygen is formed, but simply hydrogen dioxide, and it seemed probable that the oxidations were due to the compound. But Hoppe-Seyler had shown that potassium iodide and starch solution in the presence of air and palladium hydrogen are colored blue, and it is known that dilute hydrogen dioxide

<sup>1</sup> Ber. d. deutsch. chem. Gesell. 6, 106.

alone cannot effect this. He therefore suspected that the metallic palladium played a part in the reaction, and in some way acted as a carrier of oxygen from the hydrogen dioxide to the potassium iodide. The correctness of this supposition was shown as follows: After shaking palladium hydrogen for ten minutes with air and a solution of potassium iodide and starch, the solution was still colorless: that hydrogen dioxide was present was shown by adding a drop of ferrous sulphate to a portion of the colorless solution, when a heavy blue precipitate was formed. The remainder of the solution was decanted from the palladium hydrogen and poured into three flasks. To the solution in the first flask a piece of palladium foil (ignited and free from hydrogen) was added, to the second a piece of palladium hydrogen. The flasks were then completely filled and corked to exclude air. A blue color was formed only in the first flask, thus showing that metallic palladium, like platinum and ferrous sulphate, has the power of transferring oxygen from hydrogen dioxide to potassium iodide and causing the liberation of iodine. The second flask showed that palladium hydrogen has not this power, and the third flask, to which nothing had been added, showed that a dilute solution of hydrogen dioxide does not give a blue color with potassium iodide. The same results were obtained by repeating the experiment and using a solution of hydrogen dioxide prepared from barium dioxide. Hence the oxidation of potassium iodide with palladium hydrogen, observed by Hoppe-Seyler, is not due to active oxygen, but to hydrogen dioxide, which in the presence of palladium (free from hydrogen) causes the oxidation.

Traube also found that indigo-sulphuric acid was only oxidized very slowly by palladium hydrogen, which indicates that ozone is not formed, but only hydrogen dioxide, which has the power of bleaching this coloring matter very slowly. By shaking concentrated or dilute ammonia with palladium hydrogen, hydrogen dioxide was unquestionably formed; but even after the action had continued for twenty minutes, not a trace of nitrous acid could be detected in the solution. These last experiments show that palladium hydrogen with air and water forms only hydrogen dioxide, even in the presence of easily oxidized substances. Traube therefore says that Hoppe-Seyler's hypothesis of the formation of active oxygen has been refuted in all its parts, because he has shown, in the first place, that the chemical processes which take place in animal bodies are essentially different from the phenomena of decay; secondly, that hydrogen is not developed in animal tissues; thirdly, that nascent hydrogen cannot render oxygen active; and finally, that palladium hydrogen at ordinary temperatures does not give off hydrogen, neither has it the power of forming active oxygen or ozone, but in the presence of water it forms with the oxygen hydrogen dioxide alone.

E. H. K.

## ANALYTICAL CHEMISTRY.

*Hydrogen.*—A. Tschirikow.<sup>1</sup> It has been shown by W. Hempel<sup>2</sup> that hydrogen is completely absorbed by palladium sponge at 100°, and he has used this as a means of separating hydrogen from a mixture of gases. In order to test the applicability of this property to the estimation of hydrogen evolved in sealed tubes, the author treated zinc with hydrochloric acid in a sealed glass tube containing a palladium spiral. The proportions of acid and zinc were such as to produce a pressure of twenty-five atmospheres if no hydrogen were absorbed by the palladium. The absorption was found to be complete. A small portion of the hydrogen had united with the oxygen of the air remaining in the tube. Nearly the calculated amount of hydrogen was obtained from the palladium spiral by heating to 350°. The evolution of the gas was so regular that the author suggests the heating of palladium-hydrogen as a means of obtaining chemically pure hydrogen.

*Chlorine, Bromine and Iodine.*—G. Vortmann<sup>3</sup> based a method for the detection and determination of chlorine in the presence of bromine and iodine on the action of superoxides of lead and manganese on chlorides, bromides and iodides in the presence of acetic acid. Iodides are completely decomposed by either. Bromides are decomposed by lead superoxide, but not by the manganese compound. Chlorides are not attacked by either in the presence of acetic acid.

C. L. Müller and G. Kirchler,<sup>4</sup> in commenting on this method, state that chlorine is liberated when chlorides are boiled with superoxide of lead and acetic acid, either absolute or in 50 per cent. or even 10 per cent. solution. Monochloroacetic acid is also formed. Chloride of sodium is decomposed by acetic acid and manganese superoxide, but with formation of monochloroacetic acid and no free chlorine. By further decomposition, carbon dioxide, water and manganous chloride are formed. Manganese superoxide liberates bromine as well as iodine in presence of acetic acid.

In a subsequent paper<sup>5</sup> Vortmann states that his original reactions hold true when acetic acid of less than 10 per cent. strength is used. It is recommended to use a solution containing only 2–3 per cent. acetic acid. To determine the chlorine in a mixture of chlorides and bromides when the amount of bromides is small, treat with lead superoxide and evaporate to dryness two or three times. When the amount of bromine is large, or when bromides and iodides are both present, either add small portions of lead superoxide to the boiling solution, and boil for half an hour, precipitate the lead with hydrogen sulphide, and evaporate to dryness. Treat the residue with dilute acetic acid and lead superoxide, evaporate again, dissolve the residue in water, and after filtering, precipitate

<sup>1</sup> J. d. russ. phys.-chem. Gesellsch. 1882, 1, 47.

<sup>2</sup> Berichte der deutschen chemischen Gesellschaft, 12, 636.

<sup>3</sup> Ibid. 13, 325.

<sup>4</sup> Ibid. 15, 812.

<sup>5</sup> Ibid. 15, 1106; and Monatshefte für Chemie, 3, 510.

with silver nitrate. Or the iodine may be driven off by evaporating repeatedly with manganese superoxide, then, without filtering, drive off the bromine with superoxide of lead. By the second method the formation of iodic acid is avoided and it is possible to estimate each of the halogens directly.

It is very easy to determine bromine in presence of iodine by evaporating the mixture of bromides and iodides several times on a water-bath with manganese superoxide and dilute acetic acid. In order to hasten the separation of the iodine, a moderate stream of air may be passed through the solution.

**Sulphur.**—C. Winkler<sup>1</sup> has improved the *hydrogen sulphide generator*, previously described by him,<sup>2</sup> which is intended to supply large laboratories. The apparatus consists of two telescoping cylinders of lead. The outer cylinder contains dilute sulphuric acid. The inner one, which contains a shelf for the ferrous sulphide, is suspended by a chain so that it can be raised or lowered in the acid. A stop-cock in the top regulates the escape of the gas. The advantage of the apparatus is that when not in use the inner cylinder is raised out of the acid, so that the gas is not left under pressure, and there is no tendency to leak.

O. Knublauch<sup>3</sup> describes a new method for the estimation of sulphur in illuminating gas. It is a modification of that proposed by Valentin, which as improved by Tiefrunk has been used very generally. In the original method the gas was mixed with air and passed over platinum sponge in a heated platinum tube. The sulphur under these conditions is oxidized to sulphuric acid, which is absorbed in potassium carbonate and determined as barium sulphate. In Knublauch's modification a glass tube heated by a Bunsen burner is substituted for the costly platinum tube, and platinized asbestos is used. The accuracy of the method is increased by using only a slight excess of potassium carbonate, so that the barium sulphate can be washed entirely free from other salts.

For the estimation of sulphurous acid in the air Bernard Proskauer<sup>4</sup> recommends the following. The air to be examined is passed through a solution of potassium permanganate acidified with hydrochloric acid to prevent the formation of potassium hyposulphite. The excess of permanganate is reduced by oxalic acid, and the sulphuric acid resulting from the oxidation of the sulphurous acid is precipitated in the usual way. It is necessary to wash the barium sulphate with hot and moderately strong hydrochloric acid.

L. Leibermann<sup>5</sup> recommends the reaction between sulphurous acid and iodic acid as the best method of detecting the former in wines and other liquids. 15 to 20 cubic centimetres of the liquid are

<sup>1</sup> Zeitschrift für an. Chem. **21**, 386.

<sup>2</sup> *Ibid.* **15**, 285.

<sup>3</sup> *Ibid.* **21**, 335.

<sup>4</sup> Zeitschrift für an. Chem. **21**, 443.

<sup>5</sup> Berichte der deutschen chemischen Gesellschaft, **15**, 339.



distilled and a few drops of a solution of iodic acid added ; on shaking with chloroform, the violet color, due to iodine liberated by the sulphurous acid, is noticed. If the liquid contains alcohol, water must be added to the distillate to prevent the chloroform from dissolving. For quantitative estimations the wine is distilled until all the alcohol has gone over. The distillate is then diluted with water and treated with hydrochloric acid and barium chloride, to ascertain whether any sulphuric acid has been carried over. If the liquid remains clear it is slightly warmed with concentrated nitric acid in a corked flask. If the amount of sulphurous acid is at all considerable the liquid becomes turbid at once ; if only a trace, the liquid becomes turbid after standing. The reaction of Fordos and Gélis for the detection of sulphurous acid, by reduction to hydrogen sulphide by zinc and hydrochloric acid, may be used in the analysis of wines. But it is better to substitute sodium amalgam for zinc, since the latter frequently contains sulphur.

Hydrogen sulphide may also occur in wines, and it gives the same reaction with iodic acid. It may be detected independently by pouring the distillate from the wine into an alkaline solution of sodium nitro-prussiate. A violet cloud indicates the presence of hydrogen sulphide.

In the estimation of sulphuric acid, Ziegler<sup>1</sup> recommends the addition of silver nitrate after precipitation with barium chloride ; the resulting chloride of silver causes the barium sulphate to settle quickly so that it may be filtered at once. After washing the precipitate with water the chloride of silver may be removed by ammonia.

G. Lunge<sup>2</sup> recommends the use of nitric acid of specific gravity 1.42, mixed with one-third its volume of strong hydrochloric acid, for the purpose of dissolving iron pyrites. This mixture attacks the mineral much more actively than nitric acid of specific gravity 1.48.

*Nitrogen.*—As a sensitive test for gaseous ammonia G. Kroupa<sup>3</sup> recommends the use of papers saturated with fuchsine solution made yellow with sulphuric acid. They turn red with ammonia.

The ordinary method for estimating ammonia, by distilling into a receiver containing a standard solution of an acid, is open to the objection that, by irregular absorption of the ammonia, the acid occasionally runs back into the distilling flask. O. Knublauch<sup>4</sup> has arranged a receiver which is intended to avoid this difficulty. The ammonia is distilled from an ordinary flask through a glass tube connected by a rubber stopper with a glass cylinder about 40 mm. wide and open at the bottom. This dips under the surface of the standard acid contained in a beaker. The entire receiver is placed in a jar containing water that is kept cold. By this arrangement air enters the cylinder, whenever there is a tendency for the liquid to rush back toward the flask. The flask

<sup>1</sup> *Berichte der deutschen chemischen Gesellschaft*, **15**, 262.

<sup>2</sup> *Ibid.* **15**, 88.

<sup>3</sup> *Zeit. an. Chem.* **21**, 161.

<sup>4</sup> *Ibid.* **15**, 1091.

is heated rapidly from the beginning; after distilling off  $\frac{1}{4}$  to  $\frac{3}{4}$  of the liquid the glass tube is disconnected and the excess of acid titrated directly in the absorption cylinder. The method is applicable for estimating large or small quantities of ammonia and gives accurate results.

A. Jorissen<sup>1</sup> proposes to use the reaction, discovered by Vogel,<sup>2</sup> of nitrous acid on an alcoholic solution of rosaniline or fuchsine as a test for nitrous acid. It is best to use fuchsine in glacial acetic acid solution, instead of an alcoholic solution. 0.01 gram of fuchsine is dissolved in 100 cc. glacial acetic acid, and to two cubic centimetres of this solution a few drops of the liquid are added in a porcelain dish. If nitrous acid is present the liquid becomes violet, then blue, then green, and finally yellow. If a free mineral acid is added the mixture becomes yellow finally, but on adding water the original color of the fuchsine is reproduced, which is not the case when nitrous acid is present.

E. W. Davy<sup>3</sup> describes a new and expeditious method for the determination of nitrites. When an aqueous solution of gallic acid is treated with a solution of nitrous acid or a nitrite, a yellowish brown coloration results. If the amount of nitrous acid is very small the reaction is hastened by heat. One part of nitrous acid in twenty million parts of water has been detected by the author. The intensity of the color being proportional to the amount of nitrite, the method can be used for quantitative estimations in a manner analogous to the determinations of ammonia by Nessler's solution. The reaction is said to be nearly as delicate as the phenylene di-amine reaction of Griess.

W. Hempel<sup>4</sup> has investigated the methods for the preparation and analysis of nitrous oxide, and finds that Bunsen's method of analysis by exploding with hydrogen and a detonating mixture of hydrogen and oxygen, is undoubtedly the best. A mixture of 100 parts nitrous oxide with 460 parts hydrogen will not explode, whereas a mixture of 100 parts nitrous oxide with 116 parts hydrogen explodes with violence. The most favorable conditions for the analysis are to add to the nitrous oxide, two or three times its volume of hydrogen, and, in mixtures of nitrous oxide with other gases, 26 to 64 volumes of the detonating mixture to 100 volumes of non-combustible gas. The anomalous results formerly obtained with this method have been due in great measure to the difficulty in obtaining the gas in chemically pure condition. The author has not been able to prepare the gas purer than 98.8 per cent.  $N_2O$ . A small quantity of nitrogen is always present.

C. Böhmer<sup>5</sup> recommends the use of potassium permanganate and chromic acid as absorbents for nitric oxide. A saturated solution of potassium permanganate in water absorbs nitric oxide equally as well as ferrous sulphate, and has the advantage that, when used in

<sup>1</sup> Zeitsch. an. Chem. 21, 210.

<sup>2</sup> Chemical News, 46, 1.

<sup>3</sup> Zeitschrift f. an. Chem. 21, 212.

<sup>4</sup> Journ. prak. Chem. 94, 457.

<sup>5</sup> Berichte der deutschen chemischen Gesellschaft, 15, 903.

alkaline solution, carbonic acid can be absorbed at the same time. The absorption results in oxidation of the nitric oxide to nitric acid. It is aided by warming, and by its use many estimations of amido compounds, according to the method of Sachsse and Kormann, can be made in a day. If it is not required to absorb carbonic acid, chromic acid gives still better results. 1 cc. of a solution of 50 grams in 100 cubic centimetres of dilute nitric acid will absorb 18 cc. of nitric oxide rapidly.

W. Bettel<sup>1</sup> states that after removing nitrates by the copper zinc couple, the total organic nitrogen in a given solution may be estimated as ammonia (after removing free ammonia, and that from the decomposition of the nitrates) by evaporation with pure caustic soda in a copper flask of peculiar construction, finally evaporating to dryness and igniting, adding water and redistilling. When cyanides are formed on ignition, sufficient potassium permanganate is added to oxidize to cyanates. These, on adding water and boiling, are converted into ammonia.

*Phosphoric Acid.*—Zimmerman<sup>2</sup> proposed a modification of the Margueritte method for determining ferrous salts volumetrically by means of a standard solution of potassium permanganate. This modification consists in adding a solution of manganous sulphate to the ferrous solution to be determined when the latter contains hydrochloric acid. The manganous sulphate effectually prevents liberation of chlorine due to the oxidation of hydrochloric acid by the permanganate. Errors due to chlorine are thus avoided. Von der Pfordten<sup>3</sup> now applies the principle of the method as modified by Zimmerman to the determination first of molybdic and then of phosphoric acid.

Molybdic acid is determined as follows: The salt to be analyzed is dissolved in a little water, to which 60 cc. of a 27 per cent. hydrochloric acid solution are added. 8 to 10 grams of zinc in the form of sticks (the amount of iron in which has previously been determined by titration) are then introduced. When the solution has become yellow, which often results without heating, the flask is cooled before all the zinc has been dissolved, and the contents are transferred to a porcelain dish containing water, dilute sulphuric acid and manganous sulphate. (The latter salt solution is prepared by dissolving 100 grams of manganous sulphate in water and diluting to 500 cc.; 20 cc. of this solution are sufficient to prevent evolution of chlorine from 50 cc. of hydrochloric acid of specific gravity 1.12.) Potassium permanganate is now added by means of a pipette, stirring actively towards the end of the reaction, which is indicated by the appearance of a rose color. The final product of the reduction of molybdic acid is not the sesquioxide,  $M_2O_3$ , but a suboxide, which, however, by contact with the air is quickly oxidized to the sesquioxide, and, unless the air is excluded, the latter is the result of reduction.

<sup>1</sup> Chemical News, 45, 38.

<sup>2</sup> Berichte der deutschen chemischen Gesellschaft, 15, 929.

<sup>3</sup> Annalen der Chemie, 213, 314.

Phosphoric acid is determined as follows: The precipitate of ammonium phospho-molybdate is obtained in the usual way, and washed free from molybdic acid by means of a nearly saturated solution of ammonium sulphate. It is then dissolved in ammonia and diluted to a definite volume, of which a measured volume is taken which must not contain more than 0.3 gram  $\text{MoO}_3$ . Zinc and hydrochloric acid are used for reduction as above described for molybdic acid. From the amount of permanganate used the molybdic acid is determined, and from the latter the phosphoric acid by the relation  $24\text{MoO}_3$  to  $1\text{P}_2\text{O}_5$ ,

|                       |                                    |
|-----------------------|------------------------------------|
| 1 cc. $\text{KMnO}_4$ | = 0.0007585 Oxygen                 |
| 1 cc. "               | = 0.004551 $\text{MoO}_3$          |
| 1 cc. "               | = 0.0001869 $\text{P}_2\text{O}_5$ |

Good results were obtained by this method, which is applicable in all cases in which the separation of phosphoric acid by means of ammonium molybdate can take place.

D. T. D.

## NOTES.

### *Atomic Weight of Thorium.*

NILSON<sup>1</sup> has prepared pure thorium and metallic thorium, and re-determined some of their properties. The sp. g. of the metal ranges from 10.9901 to 11.0102 at  $17^\circ$ ; which gives it a molecular volume almost exactly equal to the molecular volumes of Zr, Ce, La, and Di. It was obtained as a grey powder consisting of microscopic crystals. The oxide,  $\text{ThO}_2$ , has a sp. g. of 10.22 at  $17^\circ$ . These figures are much higher than those given by previous experimenters.

The atomic weight of thorium was determined from analyses of the sulphate. The crystallized salt,  $\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$ , gave the following percentages of thorium upon ignition:

|        |
|--------|
| 45.097 |
| 45.092 |
| 45.081 |
| 45.086 |
| 45.088 |
| 45.099 |

Mean, 45.0905

Hence, if  $\text{O} = 16$  and  $\text{S} = 32$ ,  $\text{Th} = 232.43$ .

<sup>1</sup>Ber d. deutsch. chem. Gesell. 15, 2519-2547.

The anhydrous sulphate gave these percentages of  $\text{ThO}_2$  :

62.300  
62.298  
62.294  
62.298

Mean, 62.2975

Hence,  $\text{Th} = 232.37$ .

If we recalculate these data with the value for O and S given in my recent pamphlet on atomic weights,  $\text{O} = 15.9633; \pm .0035$ , and  $\text{S} = 31.984; \pm .012$ , they lead to the subjoined results:

|                         |                                     |
|-------------------------|-------------------------------------|
| From the hydrated salt, | $\text{ThO}_2 = 263.941; \pm .0394$ |
| " " anhydrous salt,     | " $= 263.959; \pm .0531$            |
| General mean,           | $\text{ThO}_2 = 263.947; \pm .0316$ |

Hence,  $\text{Th} = 232.020; \pm .0323$ .

The general mean obtained by combining all the results of Berzelius, Hermann, Chydenius, Delafontaine, and Cleve, which differed inappreciably from Cleve's results taken alone, was  $\text{Th} = 233.414; \pm .0725$ . It will be seen that Nilson's figures give a value having a much lower probable error, and that the new figure is therefore entitled to relatively very high credit. The general mean of all, including Nilson's, is  $\text{Th} = 232.262; \pm .030$ .

F. W. CLARKE.

### *Synthesis of Uric Acid.*

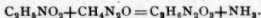
HORBACZEWSKI has succeeded in effecting the synthesis of uric acid in the following way: Pure, finely powdered glycol, obtained from hippuric acid, was mixed with ten times its weight of pure urea, prepared from ammonium cyanate, and quickly heated to  $200\text{--}230^\circ \text{C}$ . in a flask placed in a metal bath, this temperature being maintained until the fused mass, originally perfectly colorless and clear, became brownish yellow, turbid and viscid. After cooling the mass was dissolved in potassium hydroxide, the solution supersaturated with ammonium chloride, and precipitated with a mixture of an ammoniacal solution of silver and magnesia. The precipitate, which contained the uric acid, was well washed with ammoniacal water and decomposed with potassium sulphide. After the precipitate was filtered off, the filtrate was saturated with hydrochloric acid and concentrated. The product which separated on cooling was re-dissolved in dilute potassium hydroxide and twice again subjected to the same treatment. Finally there was obtained a yellowish colored crystalline powder, which was first washed with alcohol, then dried, afterward treated with

carbon bisulphide to remove sulphur, and finally treated with ether. The substance purified in this way showed all the properties and reactions of uric acid. The combustion gave results agreeing with the formula of the acid.<sup>1</sup>—(*Berichte der deutsch. chem. Gesellschaft*, **15**, 2678.)

### *The Use of Liquid Carbon Dioxide.*

A. W. HOFMANN has called attention to the extensive use of liquid carbon dioxide for various purposes. The gas is condensed and sold by F. A. Krupp of the world renowned iron works in Germany. It is used mostly to compress steel castings in closed molds. It is placed in wrought steel vessels which hold 100 kilos of the liquefied gas. A pressure of 800 atmospheres is obtained. In Krupp's works all the ice is manufactured with the aid of a machine which is kept constantly at work by compressed carbon dioxide. A large quantity of soda water used in the same works is made from liquid carbon dioxide. One of the most interesting applications of the compressed gas has been recently made in Berlin in connection with fire engines. Each engine is supplied with a large vessel containing the liquid. This is brought into use as a motor the instant the engine arrives at the place of the fire, and some of the gas is thrown with the water upon the flames. As soon as sufficient pressure of steam is obtained, the use of the carbon dioxide is stopped.—(*Berichte der deutsch. chem. Gesellschaft*, **15**, 2668.)

<sup>1</sup> The action of urea on glycol at the temperature of fusion has been studied by Griess (*Berichte der deutschen chemischen Gesellschaft*, **2**, 106), who obtained an acid of the formula  $C_2H_6N_2O_3$ :



It is, of course, possible that, at the high temperature at which Horbaczewski operated, uric acid may be formed; but, even conceding this, any rational interpretation of the reaction would be impossible, as it certainly is without analogy. The details will be awaited with impatience.

I. R.

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